Inherent safety in process plant design

An index-based approach

TECHNICAL RESEARCH CENTRE OF FINLAND ESPOO 1999

VTT PUBLICATIONS 384

Inherent Safety in Process Plant Design
An Index-Based Approach

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VTT Automation

Dissertation for the degree of Doctor of Technology to be presented with due permission for public examination and debate in Auditorium Ke2 at Helsinki University of Technology (Espoo, Finland) on the 8th of May, 1999, at 12.00 noon.

TECHNICAL RESEARCH CENTRE OF FINLAND
ESPOO 1999

ISBN 951–38–5371–3 (soft back ed.)
ISSN 1235–0621 (soft back ed.)

ISBN 951–38–5372–1 (URL: http://www.inf.vtt.fi/pdf/)
ISSN 1455–0849 (URL: http://www.inf.vtt.fi/pdf/)

JULKAISIJA – UTGIVARE – PUBLISHER

Valtion teknillinen tutkimuskeskus (VTT), Vuorimiehentie 5, PL 2000, 02044 VTT
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Technical editing Kerttu Tirronen

Libella Painopalvelu Oy, Espoo 1999

Heikkilä, Anna-Mari. Inherent safety in process plant design. An index-based approach. Espoo 1999, Technical Research Centre of Finland, VTT Publications 384. 129 p.

Keywords inherent safety, process plant design, safety analysis, case-based reasoning, genetic algorithm

Abstract

An inherently safer design is one that avoids hazards instead of controlling them, particularly by reducing the amount of hazardous material and the number of hazardous operations in the plant. Methods developed to date have largely been for the evaluating the safety of a proposed design. In the future the emphasis will be more and more on the synthesis of an inherently safer plant. At the moment it seems that the best practice is not adopted quickly enough by the potential practitioners. The aim of this work is to try to reduce this hinder by presenting an improved method for inherently safer design.

In this thesis an Inherent Safety Index for conceptual chemical process design is presented. This is required, since inherent safety should be considered in the early phases of design when the major decisions on the chemical process are made. The presented methodology allows such a consideration since the index is based on the knowledge available in the preliminary process design stage.

The total index is divided into Chemical and Process Inherent Safety Index. The previous is formed of subindices for reaction heats, flammability, explosiveness, toxicity, corrosiveness and chemical interaction. The latter is formed of subindices for inventory, process temperature, pressure and the safety of equipment and process structure.

The equipment safety subindex was developed based on accident statistics and layout data separately for isbl and osbl areas. The subindex for process structure describes the safety from the system engineering's point of view. It is evaluated by case-based reasoning on a database of good and bad design cases i.e. experience based information on recommended process configurations and accident data. This allows the reuse of existing design experience for the design of new plants, which is often neglected.

A new approach for computerized Inherent Safety Index is also presented. The index is used for the synthesis of inherently safer processes by using the index as a fitness function in the optimization of the process structure by an algorithm that is based on the combination of an genetic algorithm and case-based reasoning. Two case studies on the synthesis of inherently safer processes are given in the end.

Preface

This work was carried out at the Helsinki University of Technology in the Laboratory of Chemical Engineering and Plant Design from April 1993 to July 1998. The thesis discusses inherent safety in the conceptual process design.

I want to thank my supervisor professor Markku Hurme for his support and collaboration during this study. Dr. Jim Hawksley and Dr. Pirjo Vaija read the manuscript of this thesis and I appreciate their valuable comments. I wish to thank all members of the laboratory for creating the enjoyable working atmosphere during those years. I am especially grateful to Dr. Tuomas Koiranen who introduced me to the secrets of case-based reasoning. I thank warmly my former colleagues in VTT Automation, as well as other safety professionals I have met both in Finland and abroad, for valuable discussions and inspiration in the field of inherent safety.

The financial support provided by the Neste Foundation, the August Ramsay Foundation, the KAUTE Foundation, the Foundation of Technology, and the Academy of Finland through the Graduate School in Chemical Engineering is gratefully acknowledged.

Last but not least, I wish to express my gratitude to my family and friends for their support and understanding during the past few years. Without their encouragement this thesis would never have come to fruition.

My warmest thanks to you all!

Tampere, March 1999

Anna-Mari Heikkilä

Contents

List of symbols

CCA	Cause-Consequence Analysis
FMEA	Failure Modes and Effects Analysis
ΔH_f	heat of formation
ΔH_r	heat of reaction
HE	Hazard Evaluation
HRA	Human Reliability Analysis
I_{CI}	Chemical Inherent Safety Index
I_{COR}	Corrosiveness Subindex
I_{EQ}	Equipment Safety Subindex
I_{EX}	Explosiveness Subindex
I_{FL}	Flammability Subindex
I_I	Inventory Subindex
I_{INT}	Chemical Interaction Subindex
I_p	Process Pressure Subindex
I_{PI}	Process Inherent Safety Index
I_{RM}	Reaction Heat Subindex for Main Reaction
I_{RS}	Reaction Heat Subindex for Side Reactions

I_{ST}	Safe Process Structure Subindex
I_T	Process Temperature Subindex
I_{TI}	Total Inherent Safety Subindex
I_{TOX}	Toxic Exposure Subindex
ISBL	Inside Battery Limit Area
ISI	Inherent Safety Index
LC_{50}	Lethal Concentration 50%
LD_{50}	Lethal Dose 50%
LEL	Lower Explosion Limit
OSBL	Offsite Battery Limit Area
PHA	Preliminary Hazard Analysis
PIIS	Prototype Index of Inherent Safety
TLV	Threshold Limit Value
UEL	Upper Explosion Limit
ΔU_f	formation energies of reactants and products
ΔU_r	energy change during the reaction

1. Introduction

The aim of process design is to create a process, which is profitable, economic, safe, environmentally benign and user friendly. This is achieved by the optimization of process alternatives according to economic and functional criteria. It is required that the safety of a process plant fulfills a certain required level. This is because of general legal requirements, company image, and also due to economic reasons, since an unsafe plant cannot be profitable due to losses of production and capital.

The safety of a chemical process can be achieved through internal (inherent) and external means. The inherent safety (Kletz, 1984) is related to the intrinsic properties of the process; e.g. the use of safer chemicals and operations. The essence of the inherent safety is to avoid and remove hazards rather than to control them by added-on protective systems, which is the principle of external safety. The largest payoffs are achieved by verifying that inherent safety has been considered early and often in the process and engineering design (Lutz, 1997).

The concept of inherently safer plant has been with us now for many years. But in spite of its clear potential benefits related to safety, health and the environment (SHE), as well as the costs, there has been few applications in chemical plant design. But as Kletz (1996) has written there are hurdles to be overcome. Inherently safer design requires a basic change in approach. Instead of assuming e.g. that we can keep large quantities of hazardous materials under control we have to try and remove them. Changes in belief and the corresponding actions do not come easily.

The traditional attitude in plant design is to rely much on the added-on safety systems. Reactions from industry can be expressed by two questions (Gowland, 1996): ”How do I know if my process is designed according to inherently safe principles?” and ”Can the influence of a process change on the inherent safety of a plant be measured?”. The plants are designed in a tight time schedule by using standards and so called sound engineering practice. Lutz (1997) has realized that inherent safety alternatives has become a requirement in companies that understand that inherently safer plants have lower lifetime costs and therefore are more profitable. Chemical process industry in general overlooks the simplicity of designing to eliminate the hazard at the earliest opportunity. The result is controls being engineered near the end-point of the design and capitalization process. With this approach add-on systems become the only oppoturnities for process safety and pollution controls. Systems added late in design require continual staffing and maintenance throughout the life of the plant greatly adding to the lifetime costs as well as repetitive training and documentation upkeep.

There is no general answer to the question of which process is inherently safer. One problem is how to minimize simultaneously the risk associated with all of the process hazards. In the real world, the various hazards are not independent of each other, but are inextricably linked together (Hendershot, 1995). A process modification, which reduces one hazard, will always have some impact, positive or negative, on the risk resulting from another hazard. The advantages and disadvantages of each option must be compared for a particular case and the choice made based on the specific details of the process and materials. As an example Hendershot (1995) points out current concerns about the adverse environmental effects of chlorofluorocarbons (CFCs). It is easy to forget that these materials were originally introduced as inherently safer replacements for more hazardous refrigerants then in use. While the alternative materials are inherently safer with respect to long term environmental damage, they are often more hazardous with respect to flammability and acute toxicity.

One way of assessing the efficiency of existing safety policies is to look accident statistics in industry. They show (Anon., 1997) that in USA about 23000 accidents involving toxic chemicals took place in the period 1993 to 1995. This corresponds to an average of 7700 accidents per year. These accidents also resulted in about 60 deaths and evacuations of 41000 people. In the years 1988 to 1992 the yearly average was 6900 accidents. Thus the trend is increasing. It seems that the traditional approach of reducing risks is not enough and new types of actions are needed. This calls for more preventative strategies such as inherent-safety plant design.

To implement inherent safety in practice, a method to estimate the inherent safety of different design alternatives is needed. Methods such as Dow and Mond Indices are commonly used in chemical industry, but their point is mostly in fire and explosion hazards. They also often need detailed information on the process, while in the beginning of design there is only scarce knowledge available. In this study an Inherent Safety Index will be presented to solve the safety evaluation problems in the conceptual engineering phase.

2. Safety

According to Kharbanda and Stallworthy (1988) safety is a concept covering hazard identification, risk assessment and accident prevention. Safety should always come first and remain so despite of costs. Good design and forethought can often bring increased safety at less cost.

The best known measure for safety is risk, which is defined as the possibility of loss (Taylor, 1994). The problem of awareness of risk can be seen as one of failure of communication and of mismanagement (Kharbanda and Stallworthy, 1988). Risk by the Chartered Insurance Institute (1974) is the mathematical probability of a specified undesired event occuring, in specified circumtances or within a specified period. In a process plant the losses may be such as a damage to equipment, a loss of production or an environmental damage as well as an injury or a death. Risk involves two measurable parameters (Taylor, 1994): consequence and probability. Some events are more probable to occur than others, but a unique consequence of the sequence of events cannot be predicted.

A hazard is a condition with the potential of causing an injury or a damage (Heinrich, 1968). A chemical process normally has a number of potential hazards, for example raw material and intermediate toxicity and reactivity, energy release from chemical reactions, high temperatures, high pressures, quantity of material used etc. Each of these hazards impacts the overall process risk (Hendershot, 1995). A pursuit of safety is largely a matter of identifying hazards, eliminating them where possible or otherwise protecting against their consequences. Often two hazards need to be present simultaneously to cause a major accident. In Figure 1 Kletz (1992a) has presented the techniques for identifying hazards and the techniques for assessing those hazards.

In practice the main purpose of the process plant design is to minimize the total process risk for the limitation of effects. Here risk is the product of the probability of an incident to happen and the possible consequences of that incident. In this thesis the limitation of effects by the means of inherent safety principles is evaluated.

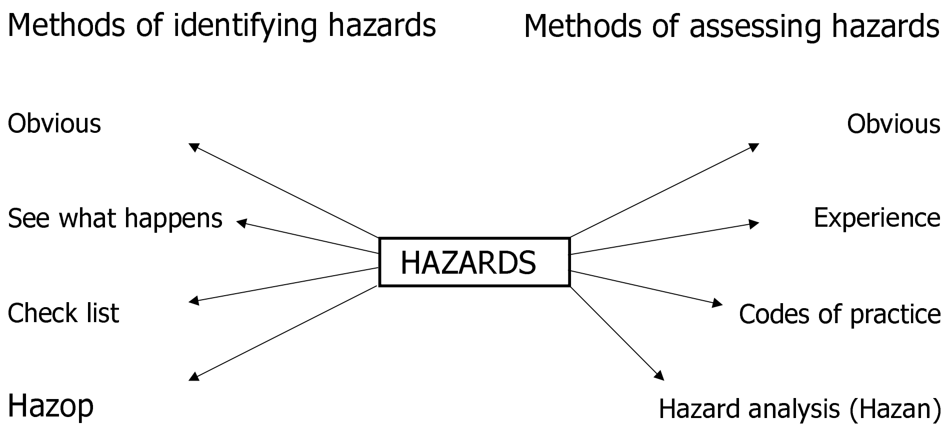

*Figure 1. Methods of identifying and assessing hazards (Kletz, 1992a)***.**

3. Evaluation of Safety

It is required that the safety of a process plant fulfills a certain required level. This is because of general legal requirements, company image, and also due to economic reasons, since an unsafe plant cannot be profitable due to losses of production and capital. Thus safety should influence design decisions from the first moments of the design project.

Safety evaluation is usually done by safety analyses methods. Safety analysis is a systematic examination of the structure and functions of a process system aimed at identifying potential accident contributors, evaluating the risk presented by them and finding risk-reducing measures (Koivisto, 1996).

It is most important that the whole life cycle of a process plant can be evaluated on safety. Safety and risk analyses evaluate the probability of a risk to appear, and the decisions of necessary preventative actions are made after results of an analysis. The aim of the risk estimation is to support the decision making on plant localization, alternative processes and plant layout. Suokas and Kakko (1993) have introduced steps of a safety and risk analysis in Figure 2. The safety and risk analysis can be done on several levels. The level on which the analysis is stopped depends on the complexity of the object for analysis and the risk potential.

Some safety analysis techniques and their typical use are presented in Figure 3 as given by CCPS (1992). It can be seen that together these hazard evaluation methods cover well the needs of the life cycle of a process plant. However this is not a complete list but also some other methods are applicable as seen in Ch. 5.

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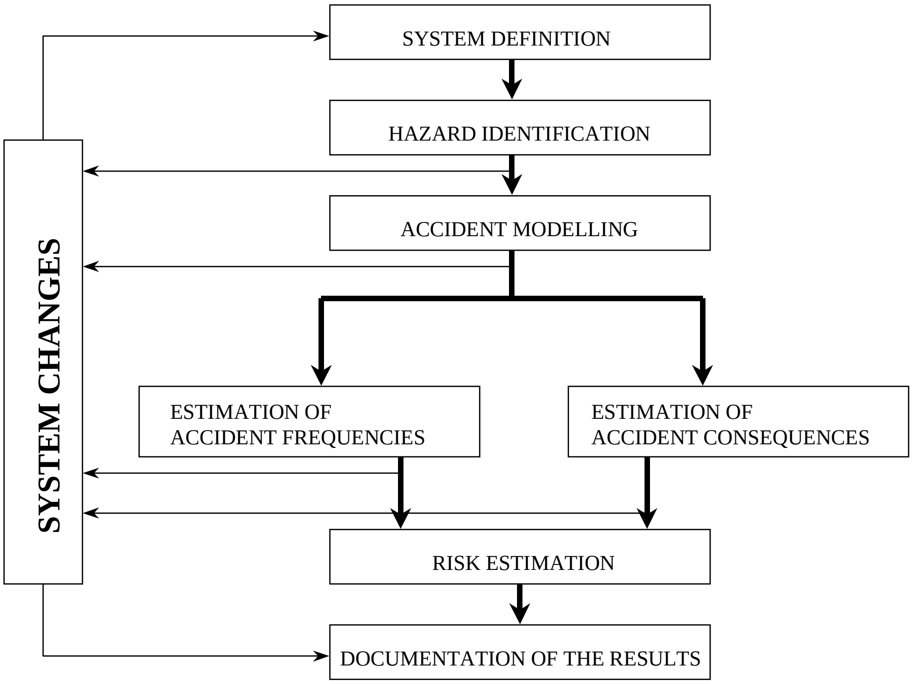

Figure 2. Steps of a safety and risk analysis (Suokas and Kakko, 1993).

There also exist many standards on safety that document the experience and define standard procedure for many recurring and similar situations. They generally conform to local and national regulations as well as to the standard practices of major engineering societies (Koivisto, 1996). Difficulties in the use of standards are e.g. their limited number and their very nature which is commonly accepted established experience. Obviously new inventions cannot immediately meet these standards. Problems also arise when undue reliance and unreasonable expectations have been created regarding safety standards.

	Safety Review	Checklist	Relative Ranking	PHA	What-If	What-if/Checklist	HAZOP	FMEA	Fault Tree	Event Tree	CCA	HRA
Research & Development	○	○	●	●	●	○	○	○	○	○	○	○
Conceptual Design	○	●	●	●	●	●	○	○	○	○	○	○
Pilot Plant Operation	○	●	○	●	●	●	●	●	●	●	●	●
Detailed Engineering	○	●	○	●	●	●	●	●	●	●	●	●
Construction/Start-up	●	●	○	○	●	●	○	○	○	○	○	●
Routine Operation	●	●	○	○	●	●	●	●	●	●	●	●
Expansion or Modification	●	●	●	●	●	●	●	●	●	●	●	●
Incident Investigation	○	○	○	○	●	○	●	●	●	●	●	●
Decommissioning	●	●	○	○	●	●	○	○	○	○	○	○

❍ Rarely used or inappropriate ● Commonly used

Figure 3. Typical Uses of Hazard Evaluation techniques (CCPS, 1992).

4. Some Safety Analysis Methods for Process Plant Design

Several safety analysis methods have been developed already. Some of them are internationally known and proved, some have been used and developed more or less inside companies. Information requirements of the methods are different, also the results produced vary. Thus different safety methods are suitable for different stages of process development, design and operation (Fig. 3). Some safety analysis methods are discussed below in more detail.

Process industry has used the Dow Fire and Explosion Hazard Index (DOW, 1987) and the Mond Index (ICI, 1985) for many years. These indices deal with fire and explosion hazard rating of process plants. Dow and Mond Indices are rapid hazard-assessment methods for use on chemical plant, during process and plant development, and in the design of plant layout. They are best suited to later design stages when process equipment, chemical substances and process conditions are known.

Another widely used safety analysis method in process industry is the Hazard and Operability Analysis, better known as Hazop (Kletz, 1992). The conventional Hazop is developed to identify probable process disturbances when complete process and instrumentation diagrams are available. Therefore it is not very applicable to conceptual process design. Kletz has also mentioned a Hazop of a flowsheet, which can be used in preliminary process design, but it is not widely used. More usable method in preliminary process design is PIIS (Edwards and Lawrence, 1993), which has been developed to select safe process routes.

Other possible preliminary safety analysis methods are concept safety review (CSR), critical examination of system safety (CE), concept hazard analysis (CHA), preliminary consequence analysis (PCA) and preliminary hazard analysis (PHA) (Wells et al., 1993). These methods are meant to be carried out from the time of the concept safety review until such time as reasonably firm process flow diagrams or early P&I diagrams are available.

CSR provides the means for an early assessment of safety, health and environmental hazards. It contributes to decisions such as siting and preferred route. CHA identifies the hazardous characteristics of the project, which are recognized in previous incidents. Hazardous characteristics embrace both hazards and hazardous conditions. CE provides an early study of the design intent of a particular processing section. It can be used either to eliminate or to reduce the possible consequences of a hazardous event. PCA is used to identify likely major accidents and to examine the impact of possible accident on a particular process plant. It is carried out as soon as a description of the process flow diagram is available. PHA is meant for the identification of applicable hazards and their possible consequences with the aim of risk reduction. PHA should be carried out at a stage when change in the design is still possible.

The Dow Fire and Explosion Hazard Index, the Mond Index, Hazop and PIIS are discussed here in more detail. The methods and their elements are also presented in Table 1.

4.1 Dow Fire and Explosion Hazard Index

The purpose of the Dow Fire and Explosion Hazard Index (Dow, 1987) is to: 1) quantify the expected damage of potential fire and explosion incidents in realistic terms, 2) identify equipment that would be likely to contribute to the creation or escalation of an incident and 3) communicate the fire and explosion risk potential to management. The Dow Index is the product of the Unit Hazard Factor and the Material Factor (Table 1).

The material factor MF for the process unit is taken of the most hazardous substance present, which lead to the analysis of the worst case that could actually occur. MF is a value, which denotes the intensity of energy release from the most hazardous material or mixture of materials present in significant quantity in the process. MF is obtained from the flammability and reactivity of the substances. The process is divided into units. The material factor is calculated for each unit separately. Dow (1987) has listed a number of chemical compounds and materials with their MF's.

The Unit Hazard Factor for process unit is the product of general and special process hazards. Penalties of general process hazards deal with different exothermic chemical reactions, endothermic processes, material handling and transfer, enclosed or indoor process units, access to the area, and drainage and spill control. Special process hazards contain the factors for toxic materials, sub-atmospheric pressure, operation in or near flammable range, dust explosion, relief pressure, low temperature, quantity of flammable and unstable materials, corrosion and erosion, leakage in the cases of joints and packing, use of fired heaters, hot oil systems and rotating equipment.

The values of the factors are determined on the basis of the Dow's Fire & Explosion Hazard Index Classification Guide (Dow, 1987). The Guide includes rules and tables, which cover well the most chemical substances and unit operations.

4.2 Mond Index

The Mond Index (ICI, 1985) has been developed from the 1973 version of the Dow F&E Index. The principal modifications to the Dow method include (Lees, 1996): 1) wider range of processes and storage installations can be studied, 2) covers processing of chemicals having explosive properties, 3) improved hazard consideration for hydrogen, 4) additional special process hazards, 5) toxicity included into the assesment.

In the Mond Index the plant is divided into individual units on the basis of the feasibility of creating separating barriers. One of the factors taken into account in the index is therefore plant layout. The potential hazard is expressed in terms of the initial value of a set of indices for fire, explosion and toxicity. A hazard factor review is then carried out to see if design changes reduce the hazard, and intermediate values of the indices are determined. Offsetting factors for preventative and protective features are applied and the final values of the indices, or offset indices, are calculated. The elements of the Mond method are listed in Table 1.

4.3 Hazard and Operability Analysis (Hazop)

Hazard and Operability Analysis (Hazop) (Kletz, 1992) is one of the most used safety analysis methods in the process industry. It is one of the simplest approaches to hazard identification. Hazop involves a vessel to vessel and a pipe to pipe review of a plant. For each vessel and pipe the possible disturbances and their potential consequences are identified. Hazop is based on guide words such as no, more, less, reverse, other than, which should be asked for every pipe and vessel (Table 1). The intention of the quide words is to stimulate the imagination, and the method relies very much on the expertise of the persons performing the analysis. The idea behind the questions is that any disturbance in a chemical plant can be described in terms of physical state variables. Hazop can be used in different stages of process design but in restricted mode. A complete Hazop study requires final process plannings with flow sheets and PID's.

Kletz (1991) has pointed out an important difference between a conventional Hazop of a line diagram (= PID) and a Hazop of a flowsheet (i.e. the process concept). In a conventional Hazop deviations from design conditions are assumed to be undesirable and ways of preventing them are looked for. Also in the Hazop of a flowsheet deviations are generated but they are actually looked for to find new process alternatives. Although many detailed accounts of conventional Hazops have been published, little or nothing has appeared concerning the detailed results of a flowsheet Hazop (compare Fig. 3, which considers Hazop as rarely used in the conceptual design). Still there is a growing interest on the flowsheet Hazop as a result of the ability to link a computerized Hazop to computer aided design systems, which allows a preliminary Hazop to be done during design. Even if the conventional Hazop is a powerful technique for identifying hazards and operating problems, it comes too late for major changes to be made.

In the forthcoming Hazop standard (IEC 61882, 1999) the Hazop studies are recommended to be carried out throughout the life cycle of a system. But for the concept and definition phase of a system's life cycle other basic methods are suggested (see Fig. 3).

4.4 Prototype Index of Inherent Safety (PIIS)

Edwards and Lawrence (1993) have developed a Prototype Index of Inherent Safety (PIIS) for process design. The inherent safety index is intended for analysing the choice of process route; i.e. the raw materials used and the sequence of the reaction steps. This method is very reaction oriented and does not consider properly the other parts of the process even they usually represent the majority of equipment.

The PIIS has been calculated as a total score, which is the sum of a chemical score and a process score (Table 1). The chemical score consists of inventory, flammability, explosiveness and toxicity. The process score includes temperature, pressure and yield. Some of the scores are based on similar tables in the Dow and Mond Indices. Others have been constructed by dividing the domain of values of a parameter into ranges and assigning a score to each range. They are supposed to be modified in the future.

It has been argued that an overall inherent safety index, such as the PIIS, incorporates some kind of build-in judgement of the relative importance of the various types of hazards. The user has to defer to the judgement of the developer of the index or has to modify it to incorporate his own judgement. In the latter case the results are not any more comparable with other users (Hendershot, 1997). Also the PIIS may be used as such or the factors may be weighted by the user. Hendershot (1997) prefers a system where contributory factors are evaluated by known indices such as the Dow F&E Index and the alternatives are compared e.g. by Kepner-Tregoe method (Kepner and Tregoe, 1981). We should keep in mind however that even Dow F&E Index includes built in judgement on the importance of terms.

The PIIS has some clear advantages over some other numerical indices in early design stages, because it can be used when the most of detailed process information is still lacking.

Table 1. The elements included into some safety analysis methods.

Safety analysis methods	**Elements of the method**
Dow Fire and Explosion Index	Material factor: • flammability and reactivity General process hazards: • exothermic chemical reactions, endothermic processes, material handling and transfer, enclosed or indoor process units, access to the area, drainage and spill control Special process hazards: • e.g. toxic materials, sub-atmospheric pressure, operation in or near flammable range, dust explosion, relief pressure, low temperature, quantity of flammable and unstable materials, corrosion and erosion, leakage in the cases of joints and packing, use of fired heaters, hot oil exchange systems, rotating equipment
Mond Index	Material factor Special material hazards General process hazards Special process hazards Quantity factor Layout hazards Toxicity hazards
Hazard and Operability Analysis (HAZOP)	Identification of process disturbances with the quide words: No, not; more, less; as well as; part of; reverse; other than; sooner, later; other place
Prototype Index of Inherent Safety (PIIS)	Chemical score: inventory, flammability, explosiveness and toxicity Process score: temperature, pressure and yield Total score: sum of the chemical and process scores

5. Limitations of the Existing Safety Analysis Methods in Conceptual Process Design

The absence of process details complicates the safety considerations. The knowledge is extended at the same time with the progress of process design. Existing safety analysis methods need different amount of information. Therefore they are suitable for different stages of the process plant design (Fig. 3). For instance most existing quantitative methods can be used first in the pilot plant phase when there is enough information (Koivisto, 1996).

The What-if, the checklists and Hazop are well publicized hazard identification tools. But as Bollinger et al. (1996) have pointed out the use of any of these techniques demands knowledge, experience and flexibility. No prescriptive set of questions or key words or list is sufficient to cover all processes, hazards and all impacted populations. Bollinger et al. find that refinement of the quantitative measurement techniques such as safety indices and convergence to a single set of accepted indices would be beneficial.

The Dow and Mond Indices and Hazop presented in Chapter 4 are widely used for the safety evaluations of process plants. They cover well those risks and hazards existing on a chemical plant. However a lot of detailed information is needed to complete those analysis. In the early stage of process design many of the required process details are still unknown. Therefore the presented safety analysis methods are not directly applicable in their full mode.

Table 2 represents the information produced in different design stages. In the preliminary design phase the available information is limited to raw materials, products, by-products, rough capacity, main phases of process and a rough range of process conditions (temperature and pressure). However in this phase of a plant design the changes for safety will be most profitable, since nothing has been built or ordered yet and thus no expensive modifications are needed.

In Table 3 there have been presented the information requirements of the safety analysis methods in Chapter 4. It can be seen by comparing the information available (Table 2) and information requirements (Table 3) that the inherent safety index methods, such as PIIS (Ch. 4) or ISI (Ch. 8), are the most suitable methods in the predesign phase. They have low information requirements compared to more detailed methods. This is because they have been developed for the situations where much of the process data is still missing.

Table 2. Safety analysis methods in the different phases of process plant design.

Design stage	**Documents produced**	**Information produced**	**Some suitable safety analyses**
Process R&D	• literature review • patent review • research reports • bench scale & pilot reports • sketch of flow sheet	• chemicals and their characteristics • chemical reactions and interactions • thermodynamics • physical properties • preliminary process concept	Laboratory screening and testing • for chemicals (toxicity, instability, explosibility) • for reactions (explosibility) • for impurities • Pilot plant tests
Predesign (Conceptual design)	• flow sheet • preliminary pid • feasibility study • preliminary operation instructions	• material balance • energy balance • process concept • operating conditions • sketch of layout	ISI, PIIS (coarse; Dow F&E Index, Mond Index, Hazop)
Basic engineering	• final flow sheets • final PID • data sheets for equipment, piping,	• process data on equipment, piping and instruments • operating, start-up and shut-down procedures	Dow F&E Index, Mond Index, Hazop, Hazan, Fault tree, RISKAT

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	instruments etc. • operating instructions • preliminary layout	• preliminary layout	
Detailed engineering	• equipment specifications • piping specifications • instrument specifications • electrical specifications • control specifications • construction specifications	• detailed engineering data for equipment, piping, instruments, controls, electrical, constructions etc. • layout	Hazop, Dow F&E Index, Mond Index, Fault tree
Procurement Fabrication Construction	• vendor and fabrication documents • inspection reports • field change documents	• vendor data on equipment • 'as built' data	What-If, Checklist
Start-up	• start-up and test-run documents	• data on process performance • first operation experience	What-If, Checklist
Operation	• operation reports	• operation data • operation experience	Hazop, Dow F&E Index, Mond Index, Fault tree

Table 3. Information required for safety analysis methods.

Chemical requirements	**Process and equipment requirements**	**Other requirements**
Dow Fire & Explosion Hazard Index (Dow, 1987)		
• self-reactivity (instability) • reactivity with water • flammability or combustibility • thermal nature of reaction • toxic materials • dust properties • corrosion rate	• a plot plan of the plant • a process flow sheet • type of process • in or near flammable range, pressure, temperature, quantity of materials, leakage - joints and packing, equipment types • loss protection (= process control, material isolation, fire protection, diking)	
Mond Index (Lees, 1996)		
• reactivity of materials • ignition sensitivity • spontaneous heating and polymerization • explosive decomposition	• type of process • material transfer • process conditions (p, T, corrosion/erosion, etc.)	

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• physical changes • toxicity	• layout distances	
Prototype Index of Inherent Safety (Edwards and Lawrence, 1993)		
• flammability • explosiveness • toxicity	• inventory • temperature • pressure • yield	
Hazard and Operability Analysis (Kletz, 1992)		
• reactions • flammability • toxicity • flash point • reaction conditions • other physical and chemical properties of materials	• flowsheets and PIDs • temperature, pressure, flow, level, composition	• carried out by a team of e.g. design and process engineer, instrument expert, research chemist and independent chairman

6. Inherent Safety

The best way of dealing with a hazard is to remove it completely. The provision of means to control the hazard is very much the second solution. As Lees (1996) has said the aim should be to design the process and plant so that they are inherently safer.

"Inherent" is defined by the American College Dictionary as "existing in something as a permanent and inseparable element, quality or attribute". Thus an inherently safer chemical process is safer because of its essential characteristics, those which belong to to the process by its very nature. An inherently safer design is one that avoids hazards instead of controlling them, particularly by removing or reducing the amount of hazardous material in the plant or the number of hazardous operations.

Inherent safety has first widely expressed in the late 1970's by Trevor Kletz. The basic principles are common sense and include avoiding the use of hazardous materials, minimising the inventories of hazardous materials and aiming for simpler processes with more bening and moderate process alternatives (Kletz, 1984).

While the basic principle of inherently safer design is generally accepted, it is not always easy to put it into practice. Inherently safer design has been advocated since the explosion at Flixborough in 1974. Progress has been real but nevertheless the concept has not been adopted nearly as rapidly as quantitative risk assessment, introduced into the chemical industry only a few years earlier (Kletz, 1996).

It has been commented that methods developed to date have largely been for evaluating the safety of some proposed design. In the future safety experts expect to see a greater emphasis on the use of knowledge to synthesize a safe plant design in the first place. In their opinion the value of inherent safety has been recognised, but there is still room for better awareness and practice. The concern expressed by inherent safety experts is that best practice is not being adopted quicly enough by the potential practitioners (Preston, 1998).

Mansfield (1994) has pointed out that in industry there is an increasing need to address and sometimes balance the overall lifecycle health, safety and environmental aspects of performance. This shows that in the real life we should talk about Inherent SHE (Safety, Environment and Health) instead of plain inherent safety. Especially in the management of safety, health and environmental protection integration of legislation (e.g. SEVESO II, OSHA Process Safety Management) and systems such as EMAS, ISO 14000 and Responsible Care are needed (Turney, 1998). Otherwise it is possible to create conflict situations. For example environmentally and economically important energy savings may lead to inherently unsafer process solutions (see Fig. 9).

6.1 The Principles of Inherent Safety

The inherent safety is the pursuit of designing hazards out of a process, as opposed to using engineering or procedural controls to mitigate risk. Therefore inherent safety strives to avoid and remove hazards rather than to control them by added-on systems. The inherent safety is best considered in the initial stages of design, when the choice of process route and concept is made.

Kletz (1984, 1991) has given Basic Principles of Inherent Safety as follows:

* *Intensification*

> "What you don't have, can't leak." Small inventories of hazardous materials reduce the consequencies of leaks. Inventories can often be reduced in almost all unit operations as well as storage. This also brings reductions in cost, while less material needs smaller vessels, structures and foundations.

* *Substitution*

> If intensification is not possible, an alternative is substitution. It may be possible to replace flammable refrigerants and heat transfer with non-flammable ones, hazardous products with safer ones, and processes that use hazardous raw materials or intermediates with processes that do not. Using a safer material in place of a hazardous one decreases the need for added-on

protective equipment and thus decreases plant cost and complexity.

* *Attenuation*

If intensification and substitution are not possible or practicable, an alternative is attenuation. This means carrying out a hazardous reaction under less hazardous conditions, or storing or transporting a hazardous material in a less hazardous form. Attenuation is sometimes the reverse of intensification, because less extreme reaction conditions may lead to a longer residence time.

* *Limitation of Effects*

If it is not possible to make plants safer by intensification, substitution or attenuation, the effects of a failure should be limited. For instance equipment is designed so that it can leak only at a low rate that is easy to stop or control. For example gaskets should be chosen to minimize leak rates. Also limitation of effects should be done by equipment design or change in reaction conditions rather than by adding on protective equipment.

**Simplification*

Simpler plants are inherently safer than complex plants, because they provide fewer opportunities for error and contain less equipment that can go wrong. Simpler plants are usually also cheaper and more user friendly.

**Change Early*

Change Early means identification of hazards as early as possible in the process design. The payback for early hazard identification can make or break the capital budget of a new process. This can be achieved by dedicated safety evaluation methodologies which are designed for preliminary process design purposes.

**Avoiding Knock-On Effects*

Safer plants are designed so that those incidents, which do occur, do not produce knock-on or domino effects. For example safer plants are provided with fire breaks between sections to restrict the spread of fire, or if flammable materials are handled, the plant is built out-of-door so that leaks can be dispersed by natural ventilation.

**Making Status Clear*

Equipment should be chosen so, that it can be easily seen, wheather it has been installed correctly or wheather it is in the open or shut position. This refers to ergonomics of the plant. Also clear explanation of the chemistry involved in the process helps operating personnel to identify possible hazards.

**Making Incorrect Assembly Impossible*

Safe plants are designed so that incorrect assembly is difficult or impossible. Assembled components must meet their design requirements. A loss of containment may result from using eg. a wrong type of gaskets.

**Tolerance*

Equipment should tolerate maloperation, poor installation or maintenance without failure. E.g. expansion loops in pipework are more tolerant to poor installation than bellows. The construction materials should be resistant to corrosion and physical conditions. For most applications metal is safer than glass or plastic.

**Ease of Control*

A process should be controlled by the use of physical principles rather than added-on control equipment (i.e. the dynamics of the process should be favourable). If a process is difficult to control, one should look for ways of changing the process or the principles of control before an investment in complex control system is made.

**Administrative Controls/Procedures*

Human error is the most frequent cause of the loss of containment. Training and certification of personnel on critical procedures are permanent considerations. Also some other inherent safety principles, like ease of control, making status clear, tolerance and making incorrect assemply impossible, come into play here.

An inherent safety design should contain the mentioned principles. They should also cover the whole design process. In the early stages of process design these principles help to choose the safest materials, process conditions and even process technology. The difficulty at the moment is the lack of rutines to implement these inherent safety principles into reality.

6.2 Inherent Safety in Preliminary Process Design

The possibility for affecting the inherent safety of a process decreases as the design proceeds and more and more engineering and financial decisions have been made (Fig. 4). It is much easier to affect the process configuration and inherent safety in the conceptual design phase than in the later phases of process design. For instance the process route selection is made in the conceptual design and it is many times difficult and expensive to change the route later. Time and money is also saved when fewer expensive safety modifications are needed and fewer added-on safety equipment are included to the final process solution.

In the early design phases the available information is limited to products, by-products and raw materials, capacity, main process equipment and a rough range of process conditions e.g. temperature and pressure. From the steps of Suokas and Kakko (1993) in Figure 2 only hazard identification can be partly done in preliminary process design. However in the early phases of a plant design the changes for safety will be most profitable, since nothing has been built or ordered yet and thus no expensive modifications are needed.

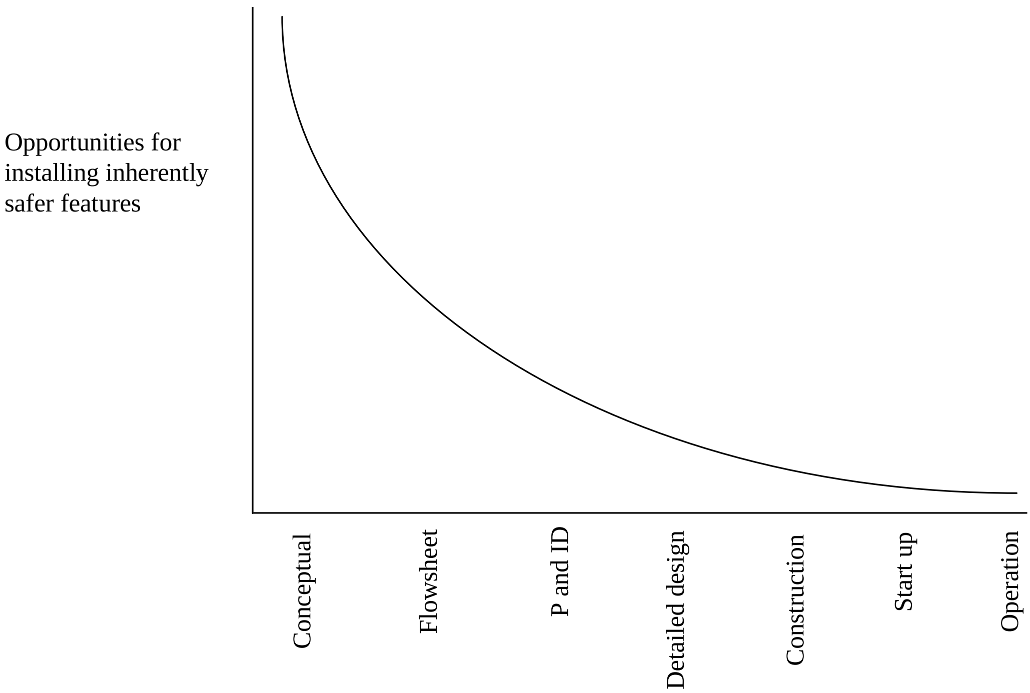

Figure 4. Inherently safer features become harder to install as a project progresses (Kletz, 1991).

6.3 Evaluation of Inherent Safety

As Hendershot (1995) has pointed out, most process options will be inherently safer with respect to one type of hazard, but may be less safe from a different viewpoint. In some cases the overall balance is readily apparent and it is easy to get general agreement on which option offers the safest overall balance. In other cases that balance is less apparent, and more sophisticated tools including qualitative ranking schemes, quantitative risk analysis and formal decision making tools may be needed.

Several authors put forward ideas for methods to be used in inherently safer design. Tools range from systematic open methods such as 'What-If' analysis (CCPS, 1992) and 'critical examination' (Wells et al., 1993), through to detailed checklists (CCPS, 1992; Hendershot, 1991; Englund, 1994; Lutz, 1994). Hendershot (1994) has proposed the use of decision analysis techniques to help address the economic, engineering and SHE factors that need to be addressed when optimising route selection and plant design. Similar approaches are being considered or used by other leading companies.

Also indices such as the Dow Fire and Explosion Hazard Index and the Mond Index have been suggested to measure the degree of inherent SHE of a process. Rushton et al. (1994) pointed out that these indices can be used for the assessment of existing plants or at the detailed design stages. They require detailed plant specifications such as the plot plan, equipment sizes, material inventories and flows. Checklists, interaction matrices, Hazop and other hazard identification tools are also usable for the evaluation, because all hazards must be identified and their potential consequences must be understood. E.g. Hazop can be used in different stages of process design but in restricted mode. A complete Hazop-study requires final process plans with flow sheets and PIDs.

The P.I.I.S. developed by Edwards and Lawrence (1993) is intended for estimating inherent safety of reaction hazards in conceotual design stage. The P.I.I.S. is intended for analysing the choice of process route i.e. the raw materials and the sequence of the reaction steps.

In the INSIDE project (INSIDE, 1997) has been developed a toolkit called InSPIRE. InSPIRE is a hyperbook development which provides chemists and engineers with the tools and methods to systematically identify, evaluate, optimise and select inherently SHE chemical processes and designs. Safety, health and environmental hazards are treated in an integrated way to ensure the conflicts and synergies between these aspects are recognised and effectively managed. The toolkit especially deals with the key early stages of a project where almost all the main decisions, which determine the SHE performance of the plant are taken. Now InSPIRE hyperbook is not readily available. At the end of the project many tools in the toolkit merit further development or validation.

There seems to be plenty of evaluation methods for inherent safety. Unfortunatelly they are not directly suitable safety analysis tools to be used with novel design systems in preliminary process design. Most existing safety analysis methods need detailed process information and are not directly applicable in early design stages. On the other hand all methods are not suitable for computerized use with optimization and simulation tools.

7. Factors Selected to Represent the Inherent Safety in Preliminary Process Design

As mentioned earlier the lack of information complicates the safety considerations in preliminary process plant design. Therefore it is important to utilize all the available details that may affect the inherent safety of the plant. To make this possible the inherent safety characteristics should be evaluated systematically during the process design. For this purpose a dedicated methodology for estimating inherent safety by using the scarce information available is required.

Most of the principles of inherent safety are useful in the preliminary design phase even most process details are still missing. This is represented in Table 4 which shows in which project phase each inherent safety feature should be considered. In fact the opportunities for installing inherent safety features decrease as the design progresses (Kletz, 1991). It can be seen from Table 4 that most features can be considered in the conceptual and flow sheet stage.

In this thesis an index based method was selected since inherent safety in formed of many subfactors which are interrelated. Therefore it is more straightforward to represent these factors as subindices which are weighted by score means as discussed later in Chapter 9.

Table 4. Project stages at which each feature of friendly design should be discussed (Kletz, 1991).

Feature	**Conceptual stage**	**Flowsheet stage**	**Line diagram stage (PID)**
Intensification	X	X	
Substitution	X	X	
Attenuation	X	X	
Limitation of effects • By equipment design • By changing reaction conditions	 X	 X	 X
Simplification	X	X	
Avoiding knock-on effects • By layout • In other ways	 X	 X X	 X
Making incorrect assembly impossible			X
Making status clear			X
Tolerance			X
Ease of control	X	X	
Software			X

The formation of inherent safety indices is based on the following principles (Fig.5): The basic principles of inherent safety (Chapter 6.1) are first described as parameters (Table 5). Most important of these parameters have been selected to be implemented as inherent safety subindices.

INHERENT SAFETY PRINCIPLES → INHERENT SAFETY PARAMETERS → INHERENT SAFETY SUBINDICES

Figure 5. Principle of the formation of the index.

Edwards and Lawrence (1993) have presented a list of sixteen chemical and physical properties and process parameters which are available at the process route selection stage (Table 5). Seven of these sixteen parameters were included to their index method (PIIS). The selected parameters concentrate very much on the chemical process route and chemistry. They have also tested their selection by an expert judgement, which gave support to their work (Edwards et al., 1996).

The intrinsic safety is however affected by *both* the process equipment and the properties of the chemical substances present in the process. Therefore also the index should reflect this fact. We have included parameters into the list (Table 5) to represent the process aspects of the inherent safety. These parameters are the type of equipment involved and the safety of process structure which describe the process configuration from a system point of view. Also a third parameter to describe the interaction (reactivity) of the chemicals present in the process has been included, since this is an obvious source of risk.

Table 5 illustrates inherent safety parameters and the selection of them by Edwards and Lawrence (1993) and Heikkilä et al. (1996). E.g. inventory has been chosen by both. It is relative to the capacity of a process and residence times (hold-up's) in vessels. It has a large effect on the degree of hazard and it should be kept small by intensification.

Phase is a release property which can be expressed also by inventory. Thus it has been excluded by us. Also reaction yield expresses inventory since higher yields decrease recycling which decreases reactor size (i.e. inventory).

Both have chosen temperature and pressure to illustrate inherent safety. This is because temperature is a direct measure of the heat energy available at release. Pressure is both a measure of the energy available at release and the energy available to cause a release.

Heat of reaction, selected by Heikkilä et al. (1996), measures the energy available from the reaction. A high heat of reaction may generate higher temperatures and dangerous runaway reactions. Another parameter to consider controllability of a reaction is reaction rate. Reaction rate does not directly express the hazardousness of a reaction (e.g. when the heat of reaction is low). Thus it has been excluded from the list of chosen parameters.

Table 5. Inherent safety parameters.

Inherent safety parameters (Edwards and Lawrence, 1993)	Chosen parameters by		Comments
	Edwards and Lawrence (1993)	Heikkilä et al. (1996)	
Inventory	x	x	relative to capacity
Phase			release property
Temperature	x	x	
Pressure	x	x	
heat of main reaction		x	high/low heat generation
new phase generation			solid/gas formation
Catalysts			
side reactions		x	heat generation
waste products			considered by substances
reaction yield	x		considered by inventory
reaction rate			considered by ΔH_R
Viscosity			hot spots
Flammability	x	x	ease of burning (liquid)
Explosiveness	x	x	explosive gas mixture
Corrosiveness		x	construction material
Toxicity	x	x	an adverse effect on the human body
chemical interaction *		x	reactivity
type of equipment *		x	choice of equipment
safety of process structure *		x	choice of configuration

*) not included to the reference Edwards and Lawrence (1993)

Chemical interaction together with heat of the side reaction expresses the potential reactiveness present in the process. The unwanted side reactions may be e.g. rapid polymerization, heat formation, and formation of flammable or toxic gas. Side reactions and possible reaction risks in the storage systems etc. are taken into account by the heat of reaction and chemical interaction.

Both have chosen flammability, explosiveness and toxicity as hazardous properties of substances. Heikkilä et al. (1996) have also included corrosiveness to the list because in corrosive environments the right choice of construction materials is essential to inherent safety.

Viscosity has not been found to be a meaningful. The hot spot effect in poorly mixed viscous reactors can be included in the heat of reaction parameter. New phase generation and catalysts have not been chosen either because both parameters are considered by hazardous properties of those substances (chemical interaction, explosiveness etc.). This applies also to waste products parameter.

The chosen meaningful parameters are the following: reaction heat, flammability, explosiveness, toxicity, corrosiveness, chemical interaction, inventory, process temperature and pressure, equipment safety and safe process structure (see Table 5). This does not mean that other factors affecting the inherent safety of a process are meaningless. On the contrary they should be considered more detailed in further design stages.

From Table 6 it can be seen how the selected parameters have a connection to the basic principles of inherent safety. For instance the subindices of equipment safety and safe process structure contain several characteristics of inherent safety such as limitation of effects or tolerance to maloperation. It is practical to include several characteristics into few parameters, since the inherent safety principles are both very broad and overlapping. The philosophy behind them cannot be described just by one process parameter. The selected parameters are discussed in more detail on the following pages.

Table 6. The characteristics of inherent safety in conceptual process design.

Principles of Inherent Safety (Kletz, 1991)	**PIIS (Edwards and Lawrence, 1993)**	**ISI (Heikkilä et al., 1996)**
Intensification - inventory - reaction volume	inventory reaction yield	inventory
Substitution - safer materials	flammability explosiveness toxicity	flammability explosiveness toxicity chemical interaction
Attenuation - lower temperature - lower pressure	temperature pressure	temperature pressure
Limitation of Effects - safer technical alternatives - safer reaction conditions	temperature pressure	equipment safety safe process structure pressure temperature chemical interaction
Simplification - simplify process facilities		safe process structure
Making Incorrect Assembly Impossible -choice of equipment, piping and fittings correctly		equipment safety safe process structure
Tolerance - resistant to maloperation		corrosiveness equipment safety safe process structure
Ease of Control		safe process structure heat of reaction

7.1 Heat of Reaction

A reaction is exothermic, if heat is generated. Reactions in which large quantities of heat or gas are released are potentially hazardous, particularly during fast decomposition or complete oxidations.

The main clue to the possible violence of any reaction lies in the heat liberated, the temperature that may be reached and the volume and nature of any gases and vapours formed. Examples of chemical characteristics that increase the potential of an explosion are high decomposition or reaction enthalpies, and high rates of energy generation. Broadly speaking, any reaction that can lead to a rise in temperature of 300°C or the production of a significant amount of gas or vapour may pose a significant hazard. (King, 1990; IChemE, 1987)

Substances with a positive enthalpy of formation release energy during their decomposition. Energetic substances can in general be identified by the presence of hazardous molecular structures like peroxide groups, nitro groups, azo groups, double and triple bonds. The presence of these groups in the molecule does not necessarily imply that the substance is hazardous (IChemE, 1987). On the other hand the initial absence of unstable groups is no guarantee for long-term stability of the compound. King (1990) has pointed out that the rates of chemical reactions often bear little or no relation to the heat or energy, which they generate. Some very fast reactions (e.g. ionic reactions in aqueous solution) produce little or no energy or heat, while others, which develope a great deal of heat, proceed very slowly in the absence of a catalyst. Thus, because the reaction rate or the presence of unstable molecular structures does not express the hazardousness of a reaction without doubt, the reaction heat has been chosen instead as a criterion.

The energy change (ΔU_r) during the reaction is equal to the difference between the energies of formation (ΔU_f) of the reactants and products:

$$\Delta U_r = \Sigma_{products}(U_f)_{products} - \Sigma_{reactants}(U_f)_{reactants} \qquad (1)$$

If the reaction occurs under isobaric conditions (constant pressure), energy can be replaced by enthalpy (ΔH_r) and the former equation can be described for constant volume conditions as follows:

$$\Delta H_r = \Sigma_{products}(H_f)_{products} - \Sigma_{reactants}(H_f)_{reactants} \qquad (2)$$

7.2 Hazardous Substances

Hazardous substances present in the process are identified on the basis of their flammability, explosiveness and toxicity. The flammability of gases and vapours of flammable liquids is a great concern in the process industries. The result of an ignition can be a fire or an explosion or both. Accidental fires and explosions of flammable mixtures with air often follow the escape of combustible materials or inlet of air into process equipment.

7.2.1 Flammability

Flammability means the ease with which a material burns in air (King, 1990). It applies to gases, liquids and solids. Flammability is very important to know for instance in the cases of leaks. The liquid which has a flash point below the processing or storage temperature can give rise to a flammable mixture and is generally considered hazardous.

The flammability of liquids depends on the lower flammability limit of the material and its vapour pressure in prevailing temperature. The flash point is the lowest temperature, at which a liquid will give off enough flammable vapour at or near its surface such, that it ignites in an intimate mixture with air and a spark or a flame. (I.e. the vapour pressure of liquid is high enough so that the concentration of gas corresponds to the lower flammability limit). Therefore the flash point is the main parameter in hazard classification of liquids and government regulations are based on these (Lees, 1996).

The boiling point may be taken as an indication of the volatility of a material. Thus, in the case of a flammable liquid also the boiling point can be a direct measure of the hazard involved in its use. (Sax, 1979)

The Finnish legislation (Pyötsiä, 1994) classifies the flammability of chemical substances on the basis of their flash and boiling points. This is similar to the European Union Directives concerning hazardous substances. Also the Dow Fire and Explosion Index (1987) and Edwards & Lawrence (1993) have been used similar approaches.

7.2.2 Explosiveness

Explosiveness means here the tendency of chemicals to form an explosive mixture in air. When an explosion occurs in atmosphere, energy is released in a short time and in a small volume so that a pressure wave which is audible is generated. Thus an explosion is a sudden and violent release of energy. The energy released in explosion derives either from physical or chemical energy. Dangers from physical energy (pressure) are considered by the pressure subindex. Therefore only chemical energy is discussed here. Chemical energy is liberated by a chemical reaction. The explosive chemicals may be either high explosives or flammable gases. The previous contain their own oxygen and do not require external oxygen to explode. They can be considered by the heat of reaction parameter. The latter are flammable (usually organic) gases which explode in excess air to yield a large volume of CO_2 and H_2O and are discussed by the explosiveness parameter.

Explosive nature of chemical substances is described with upper and lower explosion limits. The explosiveness of vapour cloud depends especially on the lower explosion limit (LEL). The LEL is the concentration of vapour, at which the vapour cloud is possible to ignite. The wider range between explosion limits means, that it is more probable that the formed vapour cloud is in the flammable region, i.e. the higher tendency for explosion. Edwards and Lawrence (1993) have used explosive limits to determine the explosiveness of chemical substances.

The use of industrial chemicals with less explosive potential makes the process more intrinsically safe. Most dangerous explosions come from large clouds of flammable material which find an ignition source. Flixborough (Lees, 1996) is an example of the destruction caused by such an incident.

7.2.3 Toxic Exposure

Marshall (1987) and Wells (1980) have described toxicity as a property of substance which destroys life or injures health when introduced into or absorbed by a living organism. The toxic hazard is a measure of the likelihood of such damage occurring. It is determined by the frequency and duration of such exposure and the concentration of the chemical in exposure.

The estimation of toxicity has been made on the basis of the animal experimentation. Toxicity of a substance depends on its physical and biological characteristics, the way of entry (in industrial context: by swallowing, through the skin, and by breathing) and the size of a dose. Also a persistent exposure of workers to relatively low levels of many industrial chemicals can produce chronic disease leading to serious disability or premature death (King, 1990). The extreme health hazards of process materials are carcinogenicity, teratology and mutagenity. Special precautions are needed in handling substances possessing these properties (Fawsett, 1982).

According to Wells (1980) probably the most commonly used toxicity term is the Threshold Limit Value (TLV), which has been defined as the concentration in air which can be breathed without harmful effect for five consecutive 8-hour working days. TLVs are based on different effects from irritation to a physiological damage. Especially in industrial context TLVs are the most usable toxicity values, while their aim is to protect employees at work. Threshold of odor is important when the TLV values are lower than the concentration of a substance needed for an odor to appear (Siegell, 1996). This is one crucial factor in emergency planning. Because legislations are usually made to protect people in general, e.g. the Finnish Legislation (Pyötsiä, 1994) uses LD_{50} and LC_{50} for toxicity. Irritation and other possible effects are dealed separately. LD_{50} is defined as the dose administered orally or by skin absorption which will cause the death of 50% of the test group within a 14-day observation period (Pyötsiä, 1994). LC_{50} is the concentration of a substance in air to which exposure for 24 hours or less would cause the death of 50% of an test group.

7.3 Corrosiveness

All metals will corrode under certain conditions. Internal corrosion is caused by galvanic corrosion, pitting, corrosion fatigue, stress corrosion cracking, stray currents, etc.

Corrosion reduces the reliability and integrity of plant. It reduces the strength of materials and causes leaks. Corrosion products affect process materials, moving parts, process efficiency and cause fouling. Corrosion proceeds slowly, and is usually more the concern of engineers than of safety professionals. Yet it has caused catastrophic failures with heavy loss of life (King, 1990).

The safety problems caused by the corrosive properties of the process streams can be prevented by a proper choice of contruction materials. The mechanical design of process is based on process design values (e.g. temperature and pressure) beyond which operation is not allowed since it can cause hazardous effects. Mechanical strength of equipment is reduced during the life of process by corrosion. Corrosion is usually measured as corrosion rates (mm/a). In the design of equipment corrosion is taken into account by the selection of material and corresponding corrosion allowance. The material is selected so that the corrosion allowance is not exceeded during the life time of the equipment. The corrosion rates are not always known during the predesign. However a rough type of material of construction is often anticipated. Since the need of better material most often indicates more corrosive conditions, a classification based on the type of construction material can be justified.

Also Dow Fire and Explosion Index (1987) considers corrosion risks, but the penalties are given through unacceptable corrosion rates. Design standards also include advice of acceptable corrosion rates (Uhlig and Reviev, 1985).

7.4 Chemical Interaction

The various chemical substances present in a process plant may in favourable conditions react with each other or with air or water causing safety or technical problems. This chemical interaction is based on the chemical reactivity of each substance with other substances present in the plant. As a potential process hazard, the chemical reactivity of any substance should be considered in the following contexts:

- reactivity with elements and compounds with which it is required to react in the process
- reactivity with athmospheric oxygen
- reactivity with water
- reactivity with itself, i.e. its propensity to polymerise, condense, decompose and explode

- reactivity with other materials, with which it may come in contact unintentionally in process, storage or transport
- reactivity with materials of construction, i.e. its corrosivity (see Chapter 7.3)

In a process, chemical interaction is either intended or unintended. The wanted reactions are under control, e.g. in the reactor. Unwanted chemical interaction can lead to unpleasant surprises like heat formation, fire, formation of harmless and nonflammable gas, formation of toxic gas, formation of flammable gas, explosion, rapid polymerization, or soluble toxic chemicals.

United States Environmental Protection Agency, EPA (Hatayama et al., 1980) has provided a matrix for determining the compatibility of hazardous wastes. Interactivity of substances has been presented with the consequences of the reaction such as heat formation, fire, rapid polymerization, formation of flammable gases etc. Also other similar matrices exist e.g. Chempat (Leggett, 1997).

7.5 Inventory

"Any material when .... present in large quantity may be classified as hazardous."
Wells (1980)

The total quantity of material to be stored is set initially by process engineering, commercial and political considerations although subsequent hazard considerations may reduce the quantity or lead to improved layout or deconcentration of storage facilities. In general large inventories in one place are unfavourable in the cases of fire or rupture of a vessel. Potential severity can be reduced by keeping inventories low, by minimizing the reactor size and by avoiding storage of potentially hazardous materials in the synthesis train (CCPS, 1995a). For instance large quantities of very toxic gases and volatile liquids was one of the major mistakes in the Bhopal accident (King, 1990). After Bhopal and several other accidents authorities has stricten the limits for the inventories of flammable gases and liquids.

The amount of a substances present in the plant (i.e. inventory) has a large effect on the degree of hazard. It is advised to use a minimum storage inventory of hazardous materials, and to construct process and storage areas away from residential or potentially residential areas.

7.6 Temperature

Operation in extreme conditions has its own problems and hazards. Extreme conditions mean usually either very low or high temperatures or pressures.

Temperature is a direct measure of the heat energy available at release (Edwards and Lawrence, 1993). Temperature is the most important factor influencing reaction rate as shown in the Arrhenius equation. In practice an increase in temperature of 10°C will increase a specific reaction rate by two to four times depending on the energy of activation (CCPS, 1995a).

The use of high temperatures in combination with high pressures greatly increases the amount of energy stored in the plant. There are severe problems with materials of construction in high temperature plants. The use of high temperatures implies that the plant is put under thermal stresses, particularly during start-up and shut-down. Also in low temperature the plant is subject to thermal stresses for the same reason. These stresses need to be allowed for and, as far as possible, avoided.

Low temperature plants contain large amounts of fluids kept in the liquid state only by pressure and temperature. If for any reason it is not possible to keep the plant cold then the liquids begin to vapourize. Another hazard in low temperature plant is possible impurities in the fluids, which are liable to come out of solution as solids. Deposited solids may be the cause not only of a blockage but also, in some cases, of an explosion.

A material of construction problem in low temperature plants is low temperature embrittlement. The material requirements are however well understood. The problems arise from the installation of incorrect materials or flow of low temperature fluids to sections of plant constructed in mild steel. These both refer to inherent safety problems.

7.7 Pressure

The use of high pressure greatly increases the amount of energy available in the plant. Whereas in an atmospheric plant stored energy is mainly chemical, in a high pressure plant there is in addition the energy of compressed permanent gases and of fluids kept in the liquid state only by the pressure. Although high pressures in themselves do not pose serious problems in the materials of construction, the combination with high temperatures, low temperatures or aggressive materials does. Thus the problem is to obtain the material strength required by high pressure operation despite these factors.

With high pressure operation the problem of leaks becomes much more serious. The amount of fluid, which can leak out through a given hole, is greater on account of the pressure difference. Moreover, the fluid may be a liquid which flashes off as the pressure is reduced.

Low (subatmospheric) pressures are not in general as hazardous as the other extreme operating conditions. But a hazard, which does exist in low pressure plant handling flammables, is the ingress of air with consequent formation of a flammable mixture. Also steam explosions may take place if a volatile material (e.g. water) is fed to a low pressure system which results to a consequent vapourization.

It is claimed that it is safer to design for total containment (Englund, 1990). This means the processing equipment to be designed to withstand the maximum pressure expected from a runaway or an other hazardous incidents. This requires detailed knowledge of the process and the possible overpressure that could result. The latter can be best obtained from the experimental data combined with a theoretical analysis. Unfortunately in many cases this information is not in hand when comparing process alternatives. In the real life it is however not often practical to construct for an emergency pressure, which can be very much higher than the normal operation pressure, therefore a relief system is nearly always required together with an added-on protective equipment such as a flare or a gas scrubber.

7.8 Equipment safety

Equipment safety tries to measure the possibility that a piece of equipment is unsafe (Heikkilä and Hurme, 1998a). Here equipment includes all major pieces of equipment such as pumps and vessels etc. but not piping, valves or instruments as separate entities. Equipment safety considers the safety of the equipment as such without interactions through the process with other equipment. This latter aspect is described by the safe process structure (Ch. 7.9). However interactions through layout, such as a furnace can be a source of ignition for a leak from other piece of equipment, are considered by the equipment safety.

The comparison of the safety of equipment is not straightforward. It depends on several features of both process and equipment themselves. It can be evaluated from quantitative accident and failure data and from engineering practice and recommendations. Experience has been used for layout recommendations and for the development of safety analysis methods such as the Dow E&F Index (Dow, 1987). Statistics contain details, causes and rates of failures of equipment and data on equipment involved in large losses.

Data on equipment involved in large losses is collected for instance by Mahoney (1997) and Instone (1989). Mahoney has analysed the 170 largest losses in refineries, petrochemical plants and gas processing plants from 1966 to 1996. Nearly all the losses in the analysis involved fires or explosions. Instone analysed some 2000 large loss claims of hydrocarbon industry at Cigna Insurance. Both gave statistical information on equipment in large losses. The difference in their data is that Mahoney has analyzed which equipment items have been the primary causes of losses whereas Instone has listed the equipment which has been involved in the losses.

During the plant design the safety of process equipment is also recognized by layout. The objectives of layout are to minimize risk to personnel, to minimize escalation (both within the plant and to adjacent plants), and to ensure adequate emergency access. It is also essential to ensure adequate access for maintenance and operations. Plant layout is a crucial factor in the safety of a process plant because of e.g. segregation of different risks, containment of accidents and limitation of exposure. Safe plant layout is designed on the basis of design standards and local regulations. Also appropriate spacing of unit operations within a process is considered inherently safer solution (Bollinger et al., 1996).

The spacing recommendations for process layout have been presented in literature as matrixes and lists of the typical minimum distances between different process items (Industrial Risk Insurers (1991); Bausbacher and Hunt (1993); Prugh (1982)). A suitable distance to another process item depends mostly on the safety properties of the process items. The clearance required for maintenance and access determine usually shorter spacings compared to safety clearances. In some references access and maintenance clearances are given separately. Therefore it can be assumed that the average of the recommended equipment spacings is mostly related to the general unsafety of a specific process item.

The frequently used Dow Fire & Explosion Hazard Index (1987) gives penalties for fired equipment and certain specified rotating equipment. These are a part of the Special Process Hazards term of the Dow Index.

There is also a certain amount of statistical information available on the failures of process system components. Arulanantham and Lees (1981) have studied pressure vessel and fired heater failures in process plants such as olefins plants. They define failure as a condition in which a crack, leak or other defect has developed in the equipment to the extent that repair or replacement is required, a definition which includes some of the potentially dangerous as well as all catastrophic failures. The failure rates of equipment are related to some extent to the safety of process items. If a piece of equipment has a long history of failures, it may cause safety problems in the future. Therefore it would be better to consider another equipment instead. It should be remembered that all reliability or failure information does not express safety directly, since all failures are not dangerous and not all accidents are due to failures of equipment.

7.9 Safe Process Structure

Safe process structure describes the inherent safety of the process configurations. The safe process structure means which operations are involved in the process and how they are connected together. Therefore the safe process structure describes the safety of the process from system engineering point of view. It describes: how well certain unit operations or other process items work together, how they should be connected and controlled together. It also describes how auxiliary systems such as cooling, heating or relief systems should be configured and connected to the main process (Heikkilä et al., 1998). The importance of this subindex is increasing as the processes are becoming more integrated through heat and mass-transfer networks.

Most factors affecting inherent safety are quite straightforward to estimate since they are e.g. based on the physical and chemical properties of the compounds present. An inherently safe process structure is not possible to define by explicit rules, but one has to rely on standards, recommendations and accident reports. This information is based on the experience gained in the operation practice of different processes (Lees, 1996). For example accident reports, which are made after accidents, give valuable information of the possible weaknesses in the different process solutions. Also extensive databases have been collected from accident reports (Anon, 1996). From this data a database of good and bad designs can be collected.

Since an inherently safe process structure cannot be described as explicit rules the reasoning has to be based on analogies. I.e. the current design is compared, if it resembles known safe or unsafe design cases in the database. This same approach is used mentally by practising engineers to generate new process designs. When this type of reasoning is computerized it is called case-based reasoning (Gonzalez and Dankel, 1993).

8. Inherent Safety Index

8.1 Total Index as an Approach

Most process selections involve tradeoffs between different inherent safety principles. I.e. one process option is inherently safer with respect to one hazard but less safe with regard to another. Therefore there has to be a way of making a total comparison of all safety aspects together. There are two basic approaches for this. The different aspects are evaluated separately and then compared by using a suitable tool (Hendershot, 1997). One possible tool which is often used in practical comparisons in preliminary process design is the Kepner-Tregoe method (Kepner and Tregoe, 1981). More decision tools are discussed by CCPS (1995b).

Another approach is to calculate an overall index value as it was done by Edwards and Lawrence (1993). This method has been criticized for including built in judgements of the developers of the index on the relative importance of the terms (Hendershot, 1997). However some kind of judgement (weighting) of the terms is needed, if a total index value is wanted. Otherwise the comparability of different total index values is lost, if the weighting is modified on case by case basis. One has to remember that also "standard indices" such as the Dow F&E Index includes much built in judgement. This can be even useful if the weighting is well justified. And when using an overall index approach the comparison of subindices can be used for comparisons when desired.

8.2 Calculation Method of the Index

In the Chapter 7 the selected inherent safety parameters for conceptual process design were presented. From these parameters an inherent safety index is formed in this Chapter. There is a straight link between inherent safety principles and the inherent safety index as discussed earlier (see Figure 5).

The inherent safety factors in Chapter 7 illustrate both chemical and process engineering aspects of inherent safety. The factors can be divided into two groups so that the first one contains all factors based on chemistry and the other group includes process engineering aspects such as equipment safety, inventory, process conditions and safe process structure (Table 7). Heikkilä et al. (1996) have based their inherent safety index on this division.

Table 7. Inherent safety index and its subindices (Hurme and Heikkilä, 1998).

Total inherent safety index	
Chemical inherent safety index	Process inherent safety index
Subindices for reaction hazards	Subindices for process conditions
Heat of the main reaction	Inventory
Heat of the side reactions	Process temperature
Chemical interaction	Process pressure
Subindices for hazardous substances	Subindices for process system
Flammability	Equipment
Explosiveness	Process structure
Toxicity	
Corrosivity	

The ISI is calculated by Equation 3, where the Total Inherent Safety Index (I_{TI}) is the sum of the Chemical Inherent Safety Index (I_{CI}) and the Process Inherent Safety Index (I_{PI}). These indices are calculated for each process alternative separately and the results are compared with each other. Table 8 describes the symbols of the subindices.

$$I_{TI} = I_{CI} + I_{PI} \tag{3}$$

The Chemical Inherent Safety Index I_{CI} (Eq.4) contains chemical factors affecting the inherent safety of processes. These factors consist of chemical reactivity, flammability, explosiveness, toxicity and corrosiveness of chemical substances present in the process. Flammability, explosiveness and toxicity are determined separately for each substance in the process. Chemical reactivity consists of both the maximum values of indices for heats of main and side reaction and the maximum value of chemical interaction which describes the unintended reactions between chemical substances present in the process area studied.

$$I_{CI} = I_{RM, max} + I_{RS, max} + I_{INT, max} + (I_{FL} + I_{EX} + I_{TOX})_{max} + I_{COR, max} \tag{4}$$

The Process Inherent Safety Index I_{PI} (Eq.5) expresses the inherent safety of the process itself. It contains subindices of inventory, process temperature and pressure, equipment safety and safe process structure.

$$I_{PI} = I_I + I_{T, max} + I_{p, max} + I_{EQ, max} + I_{ST, max} \tag{5}$$

The calculations of the Inherent Safety Index (ISI) are made on the basis of the worst situation. The approach of the worst case describes the most risky situation that can appear. A low index value represents an inherently safer process. In the calculations the greatest sum of flammability, explosiveness and toxic exposure subindices is used. For inventory and process temperature and pressure the maximum expected values are used. The worst possible interaction between chemical substances or pieces of equipment and the worst process structure give the values of these subindices.

The way of using the index is flexible. Comparisons can be made at the level of process, subprocess, subsystem, or considering only part of the factors (e.g. only process oriented factors). Different process alternatives can be compared with each other on the basis of the ISI. Also the designs of process sections can be compared in terms of their indices in order to find the most vulnerable point in the design. Sometimes a comparison based on only one or two criteria is interesting. E.g. a toxicity hazard study can be done by considering only the toxic exposure subindex. Because its flexibility the total inherent safety index is quite easily integrated to simulation and optimization tools.

It is also very important to understand that process may be inherently safe with respect to one criteria, but unsafe in another point of view. Two processes may seem equally safe in terms of the total ISI, but the scores of the subindices differ. In every case all subindices and their impact to the overall safety must be studied before the decision making.

9. The Weighting between Subindices of Inherent Safety Index

All process design projects are unique. The number and the type of the possible process alternatives vary. Also process designers may emphasize the safety factors differently according to the company policy and the problem in hand. Thus the subindices of the ISI can be weighted to fit the new situations. This can be done by introducing weighting factors to Equations 3–5 and thereby modifying the standard scores of Table 8. If the process designer prefers to use the ISI with changed weighting factors, he must use same approach to all his alternatives to make sure that all the alternatives are compared on the same basis. It is also possible to fit the ISI into the company policy by generating a standardized in-house weighting which will be then used by all employees.

In Table 8 the score domain vary from one subindex to another. The range of the scores reflects the importance of the specific subindex to the plant safety. This choice was made on the basis of the inquiry of Edwards et al. (1996). Eight experts from different fields of process safety were asked, which inherent safety aspects they considered most relevant. The experts both named the parameters, which they considered essential for assessing inherent safety and gave a score for each parameter to represent its relative importance.

Lawrence (1996) summarized the answers of the experts and calculated the total scores for each parameter. According to this summary the most important parameters for inherent safety were inventory and toxicity. Other important factors were, in this order, chemical stability, temperature, pressure, flammability and explosiveness, which were considered to be essential by all experts. Also flash points and side reactions were quite important.

We have utilized the results of this expert assessment with our own judgement to obtain the score ranges in Table 8. A wider range means greater impact to the plant safety. In our method toxicity and inventory are scored to be the most significant to the inherent safety (max scores 6 and 5). This is in agreement with the expert assessment except the safe process structure which was not included at all by the group of experts. The most other subindices were given score 4. Also this is in agreement with the expert assessment except the experts did not consider equipment safety at all. The absence of equipment safety and safe process structure in the expert assessment is probably because the experts were given a list of keywords they were asked to comment. This list did not include any equipment or process configuration oriented keywords (Lawrence, 1996).

Corrosion was given the lowest ranking (2) in the ISI, since it can be usually controlled by a proper choice of construction materials. This was also recognized by the experts.

Table 8. Inherent safety subindices.

Chemical inherent safety index, I_{CI}	**Symbol**	**Score**
Heat of main reaction	I_{RM}	0–4
Heat of side reaction, max	I_{RS}	0–4
Chemical interaction	I_{INT}	0–4
Flammability	I_{FL}	0–4
Explosiveness	I_{EX}	0–4
Toxic exposure	I_{TOX}	0–6
Corrosiveness	I_{COR}	0–2
Process inherent safety index, I_{PI}		
Inventory	I_I	0–5
Process temperature	I_T	0–4
Process pressure	I_p	0–4
Equipment safety	I_{EQ}	
Isbl		0–4
Osbl		0–3
Safe process structure	I_{ST}	0–5

10. Subindices of Chemical Inherent Safety Index

The Chemical Inherent Safety Index deals with the hazards which are related to the chemical properties of substances in the process. The Index has been divided into subindices for reaction hazards and hazardous substances.

10.1 Subindices of Reaction Hazards

The Inherent Safety Index (ISI) deals with both main reaction(s) and those side reactions taking place in the reactor and which are meaningful. It also deals with chemical interaction which describes unintentional chemical reactions which can take place among chemicals in the plant.

10.1.1 Reaction Heat Subindex for the Main Reaction

Since the possible violence of reactions lies in the heat liberated and the temperature which may be reached, the energy change during the reaction has been selected to present the reaction safety in the ISI. This is a feasible approach since the formation enthalpies are known for most substances.

The enthalpy released or absorbed in a process can be described by Equation 6 for constant volume conditions and an isobaric process. While determining the safety subindex I_{RM} the heat release of the main reaction is calculated for the total reaction mass (i.e. both the reactants and diluents are included) to take account the heat capacity of the system which absorbs part of the energy released:

$$\Delta H_r = \Sigma_{products} (H_f)_{products} - \Sigma_{reactants} (H_f)_{reactants} \qquad (6)$$

From the safety point of view it is important to know, how exothermic the reaction is. The classification used by King (1990) is following: the reaction is extremely exothermic ($\geq$ 3000 J/g), strongly exothermic (< 3000 J/g), moderately exothermic (< 1200 J/g), mildly exothermic (< 600 J/g), thermally neutral ($\leq$ 200 J/g) or endothermic. These values have also been used for determining the scores of the subindices I_{RM} and I_{RS} (Table 9). If there are several main reactions, for instance a series reaction, the score of I_{RM} is determined on the basis of the total reaction. If there are several reactors in the process under consideration, the score is determined on the reactor with the greatest heat release.

Table 9. Determination of the Reaction Heat Subindices I_{RM} and I_{RS}.

Heat of reaction/total reaction mass	**Score**
Thermally neutral ≤ 200 J/g	0
Mildly exothermic <600 J/g	1
Moderately exothermic <1200 J/g	2
Strongly exothermic <3000 J/g	3
Extremely exothermic ≥ 3000 J/g	4

10.1.2 Reaction Heat Subindex for the Side Reactions

The subindex I_{RS} of the heat of side reactions is determined in the similar way as the subindex I_{RM} for the main reaction. The heat release for each possible side reactions is calculated according to Equation 6 for the full reaction mass including diluents. The same safety scores that were used for the main reaction are utilized also for the side reations (Table 9). The greatest heat of reaction value of all side reactions is used for determining the value of the I_{RS}.

10.1.3 Chemical Interaction Subindex

Chemical interaction considers the unwanted reactions of process substances with materials in the plant area. These reactions are not expected to take place in the reactor and therefore they are not discussed in the side reaction subindex. The Inherent Safety Index has utilized EPA's matrix (Hatayama et al., 1980) to classify the hazards of the chemical interaction in a process. The worst interaction that appears between the substances present in the plant area is used in the calculations for the Chemical Inherent Safety Index.

In Table 10 the score limits for the Chemical Interaction Subindex are from 0 to

4. Fire and explosion are considered most hazardous consequences of an interaction with the score 4. The score value for the formation of toxic or flammable gas depends on the amount and the harmfulness of the gas (score 2–3). Likewise the more heat is formed the higher the score value is (score 1–3). Rapid polymerization is valued on the basis of the polymerization rate (score 2–3). Soluble toxic chemicals and formation of harmless, nonflammable gases are considered less harmful compared with others, thus score 1.

Table 10. Determination of the Chemical Interaction Subindex I_{INT}.

Chemical interaction	**Score of I_{INT}**
Heat formation	1–3
Fire	4
Formation of harmless, nonflammable gas	1
Formation of toxic gas	2–3
Formation of flammable gas	2–3
Explosion	4
Rapid polymerization	2–3
Soluble toxic chemicals	1

10.2 Subindices for Hazardous Substances

Flammability, Explosiveness and Toxic Exposure Subindices (I_{FL} , I_{EX} and I_{TOX}) are determined for each substance present in the process. These indices are summed for every substance separately. The maximum sum is used as the subindex value. Corrosiveness Subindex is determined on the basis of the most corrosive material in process.

10.2.1 Flammability Subindex

The subindex of flammability describes the flammability of liquid e.g. in the case of a leakage. Flammability of liquids is measured by their flash points and boiling points. The classification used is based on the EU directive (Pyötsiä, 1994). Substances are divided into non-combustible, combustible, flammable, easily flammable and very flammable (Table 11).

Table 11. Determination of the Flammability Subindex I_{FL}.

Flammability	**Score of I_{FL}**
Nonflammable	0
Combustible (flash point >55°C)	1
Flammable (flash point ≤ 55°C)	2
Easily flammable (flash point <21°C)	3
Very flammable (flash point <0°C & boiling point ≤ 35°C)	4

10.2.2 Explosiveness Subindex

In the ISI the explosiveness is considered through a chemical property which is not directly same as the process explosion hazard, but can be a fire estimate. Subindex of explosiveness describes the tendency of gas to form an explosive mixture with air. Explosive ranges expressed "in per cent by volume" of fuel vapour in air are the ranges of concentration of vapour or gas mixture with air which will burn when ignited. If a mixture within its explosive range of concentration is ignited, flame propagation will occur. The range will be indigated by LEL for the lower explosive limit or UEL for the upper explosive limit. This model is a coarse estimation but usefull when most chemical properties are not available.

The explosiveness is determined by the difference between the upper and the lower explosion limits of the substances. The range of explosion limits has been divided into four steps. The subindex values are shown in Table 12.

Table 12. Determination of the Explosiveness Subindex I_{EX}.

Explosiveness (UEL-LEL) vol%	**Score of I_{EX}**
Non explosive	0
0–20	1
20–45	2
45–70	3
70–100	4

10.2.3 Toxic Exposure Subindex

Health hazards caused by chemicals are represented by the Toxic Exposure Subindex (I_{TOX}). In the ISI the evaluation of toxic exposure is based on the Threshold Limit Values (TLV) because TLV data is readily available for most substances in process industry. TLV values express the harmful exposure limits of substances in the threshold time of 8 hours. The index value is higher, when the TLV is lower i.e. the substance is more toxic. It is important to use TLVs with same threshold time so that the results are comparable. Score limits in Table 13 are based on Mond Index (ICI, 1985).

Table 13. Determination of the Toxic Exposure Subindex I_{TOX}.

Toxic limit (ppm)	**Score of I_{TOX}**
TLV > 10000	0
TLV ≤ 10000	1
TLV ≤ 1000	2
TLV ≤ 100	3
TLV ≤ 10	4
TLV ≤ 1	5
TLV ≤ 0.1	6

10.2.4 Corrosiveness Subindex

Corrosive materials include e.g. acids, acid anhydrides, and alkalies. Such materials often corrode pipes, vessels and other process equipment, which may result to a loss of containment and subsequent fire, explosion or toxic release. Danger from leaks depend on the properties of the fluids. Some of the corrosive fluids are volatile, flammable and toxic, some react violently with moisture. Strong acids and alkalies will cause burns and eye damages to personnel.

Corrosion is usually measured as corrosion rates mm/a. The material is selected so that the corrosion allowance is not exceeded during the life time of the equipment. However the corrosion rates are not always known during the predesign. Still a rough type of material of construction is often anticipated. Since the need of better material most often indicates more corrosive conditions, a classification based on type of construction material can be justified.

In the Inherent Safety Index corrosiveness is determined on the basis of the required construction material (Table 14). If carbon steel is enough, the index value is 0. For stainless steel the value is 1, but for all special materials the index is 2. The estimation is made for each process stream separately, and the worst case gives the final index value.

Table 14. Determination of the Corrosiveness Subindex I_{COR}.

Construction material required	**Score of I_{COR}**
Carbon steel	0
Stainless steel	1
Better material needed	2

11. Subindices for Process Inherent Safety Index

The Process Inherent Safety Index expresses the inherent safety of the process itself including the equipment and operating parameters. The Index has been divided into subindices for inventory, temperature, pressure, equipment safety and safe process structure.

11.1 Inventory Subindex

An exact calculation of inventory is difficult in the conceptual design phase, since the size of equipment is not usually known. The mass flows in the process are however known from the design capasity of the process. Therefore it is practical to base the estimation of inventory on mass flows and an estimated residence time. Consequently the inventory has been included to the ISI as a mass flow in the ISBL equipment including recycles with one hour nominal residence time for each process vessel (e.g. reactor, distillation column etc). For large storage tanks the size should be estimated. The total inventory is the sum of inventories of all process vessels.

For OSBL area the tank sizes are normally not known in conceptual design, which means that the OSBL inventory cannot be readily calculated. The OSBL inventory is not only dependent on the ISBL process type but also local conditions, logistics etc.

For OSBL inventory values based on Mond Index (ICI, 1985) were used. These were used also for ISBL by Edwards et al. (1993) but the experts criticized this, since the relevant inventory scale in ISBL is much smaller (Lawrence, 1996). Also due to a tighter layout the same inventory in ISBL is more dangerous than in OSBL. Therefore a new scale was developed by scaling the Mond values by using the expert recommendations in Lawrence's work (1996). See Table 15.

Table 15. Determination of the Inventory Subindex I_I.

Inventory		**Score of I_I**
ISBL	**OSBL**	
0–1 t	0–10 t	0
1–10 t	10–100 t	1
10–50 t	100–500 t	2
50–200 t	500–2000 t	3
200–500 t	2000–5000 t	4
500–1000 t	5000–10000 t	5

11.2 Process Temperature Subindex

Temperature is an indicator of the heat energy in the system. The hazard increases in higher temperatures because of the energy content itself and also because the strength of materials becomes weeker in high or very low temperatures. Great temperature changes between ambient (i.e. shut down) and operating temperatures also cause thermal stress which may cause an increased hazard for a loss of containment.

Process temperature for the Inherent Safety Index (ISI) is determined on the basis of the maximum temperature in the process area under investigation. This is feasible since in the early stage of process design preliminary estimates of temperatures and pressures are available.

Because the hazards in low temperature range are increased due to mechanical problems and freezing if water is present, the temperatures below 0°C are also included to the index. When there are many temperature levels present in the process area under study, the highest temperature subindex value is applied.

The temperature ranges have been chosen on the basis of the danger to humans and on the basis of material strength as a function of temperature. For instance temperature between 0°C and 70°C is harmless to people in general. The temperature range between 70°C and 150°C is a typical temperature range for mild temperature processes. The next limit for temperature is 300°C, beyond which the strength of carbon steel is decreased considerably compared to room temperature. Materials with better heat-resistance are needed in higher temperatures. Also subzero temperatures cause problems as explained in Chapter 7.6.

Table 16. Determination of the Process Temperature Subindex I_T.

Process temperature	**Score of I_T**
< 0 °C	1
0–70 °C	0
70–150 °C	1
150–300 °C	2
300–600 °C	3
>600 °C	4

11.3 Process Pressure Subindex

Pressure is an indicator of potential energy which affects the leak rates in the case of loss of containment. Higher pressures also pose stricter requirements to the strength of vessels. Leaks in vacuum equipment may cause inlet of air and consequent explosion.

In the Inherent Safety Index (ISI) the process pressure is determined on the basis of the maximum pressure in the process area under normal operation. In the preliminary process design estimates of pressure levels are available. The pressure limits in Table 17 are based on the Dow E&F Index (Dow, 1987).

Table 17. Determination of the Process Pressure Subindex I_p.

Process pressure	Score of I_p
0.5–5 bar	0
0–0.5 or 5–25 bar	1
25–50 bar	2
50–200 bar	3
200–1000 bar	4

11.4 Equipment Safety Subindex

The Equipment Safety Subindex has been included into the ISI to get a better view of total inherent safety by discussing also the selection and the type of equipment used (Heikkilä and Hurme, 1998a and 1998b). Equipment safety tries to measure the possibility that a piece of equipment is unsafe. Here equipment includes all major pieces of equipment such as pumps and vessels etc. but not piping, valves or instruments. For instance piping or instrumentation have not been designed yet in the early design stages. Equipment safety index considers the safety of the equipment as such without interactions through the process with other equipment. This latter aspect is described by the safe process structure subindex. However interactions through layout, such as a furnace can be a source of ignition for a leak from other piece of equipment, are considered by the equipment safety index.

The main failure of equipment is a loss of process containment. The consequences depend on the properties and the amount of the leaking material and the conditions both inside and outside of process equipment. Pumps and compressors (Marshall, 1987) are perhaps the most vulnerable items of pressurised systems, because they contain moving parts and they are also subject to erosion and cavitation. Pumps and compressors produce also vibration, which may lead to fatigue failure. Both seals and bearings of pumps and compressors are liable to failure. In addition agitator systems present difficulties due to mechanical stresses, though they operate at much lower speeds than pumps.

11.4.1 Evaluation of Equipment Safety

The comparison of the safety of equipment is not straightforward. It depends on equipment themselves and process conditions. Equipment safety can be evaluated from quantitative accident and failure data and from engineering practice and recommendations. Experience-based information is found from layout recommendations and safety analysis methods such as the Dow E&F Index (1987). Quantitative data can be found from accident and operational statistics. It should be remembered that all reliability or failure information does not express safety directly, since all failures are not dangerous and not all accidents are due to failures of equipment.

For the Equipment Safety Subindex the process plant area is divided into two different areas, which have different safety properties. The onsite area is the area where the raw materials are converted into the products. This is referred as the inside battery limits area (ISBL). This area is characterized by large number of equipment and piping located in a concentrated way in a small area. The rest of the plant is referred as the offsite or outside battery limits area (OSBL). The offsite area is characterized by large inventories of fluids, which are often flammable and/or toxic. The number of equipment in OSBL area is smaller but their size larger than in the ISBL area. The layout is much more scattered in OSBL than in ISBL which is to enhance safety.

11.4.2 Equipment Layout

During the plant design the safety of process equipment is also recognized by layout. The objectives of layout are to minimize risk to personnel, to minimize escalation (both within the plant and to adjacent plants), and to ensure adequate emergency access. It is also essential to ensure adequate access for maintenance and operations.

Plant layout is a crucial factor in the safety of a process plant because of e.g. segregation of different risks, containment of accidents and limitation of exposure. Safe plant layout is designed on the basis of design standards and local regulations. These are often expressed as minimum clearances between equipment. Safety distances between plant items can in principle be calculated by estimating the size of possible leaks, the probability of ignition and explosion and their effects. Since this approach is full of difficulties, experience based minimum distances are used instead (Wells, 1980). Even though process layouts are not available in the preliminary process design the spacing recommendations give an idea of the risk of certain pieces of equipment to their environment.

Layout spacings are also affected by other factors than safety. The space requirements of maintenance, repair works and proper performing of process operations has to be included into the process layout. Proper spacing around equipment is required to allow easy operation. Enough room should be provided for pipes, supports and foundations as well.

The spacing recommendations for process layout have been presented in literature as matrixes and lists of the typical minimum distances. In this work the equipment spacing matrixes of Industrial Risk Insurers (1991), Bausbacher and Hunt (1993), Prugh (1982), Mecklenburgh (1985) and Institut Francais du Petrole have been compared. A suitable distance to another process item depends mostly on the safety properties of the process items. The clearance required for maintenance and access determine usually shorter spacings compared to safety clearances. In some references access and maintenance clearances are given separately. Therefore it was assumed that the average of the recommended equipment spacings is mostly related to the general unsafety of a specific process item and not to the maintenance etc. aspects.

The evaluation of the layout spacing data was done by calculating the averages of the recommended equipment spacings. In some matrixes the spacings for operational and maintenance access were not included, in which case a minimum distance of one metre has been used. It was noticed that the order of the process items according to their average spacing requirements is almost identical in all referred matrixes. For ISBL layout (Table 18) e.g. furnaces, compressors and high hazard reactors were on the top of the lists, while equipment handling nonflammable and nontoxic materials were in the other end. The former needed extra spacing for safety and the latter required only enough room for operation, repair and maintenance. The exception to the rule is the higher ranking of towers in the matrix of Industrial Risk Insurers (1991). This is probably because of the the large inventory of material, which leads to large economical losses in a case of rupture.

Table 18. Comparison of the average spacing recommendations for some ISBL process items.

Equipment items	**Average equipment spacing in metres by**			
	Prugh (1982)	Bausbacher and Hunt (1993)	Industrial Risk Insurers (1991)	Institut Francais du Petrole
Furnaces	15.3	11	15.7	13.2
Compressors	9.6	4.6	14.2	9.1
Reactors (high hazard)*	8.9		11	
Air coolers	8.1	4.4	10	5.4
Reactors	8	4.2	9.2	5.4
Pumps (high hazard)*	8.8	4.1	8.2	5.3
Towers, drums	7.7 / 7.2	3.2	10	4.0 / 2.8
Heat exchangers	7.5–6.6	2.3	7.8	4.9–3.6
Pumps (light ends/normal)	7.7 / 6.3		7	4.6 / 4.3
Equipment handling non-flammables	1.7	min (= 1m)		1.6

* the high hazard reactors and pumps refer to process items handling materials above their autoignition point, whereas conventional pumps and reactors handle materials below their autoignition point.

The calculated average spacing recommendations for OSBL equipment are given in Table 19. It can be seen that the order of the process items according to their average spacing requirements is quite similar in all matrices. Flares are given clearly the largest spacing recommendations. The aim of the long distances is to prevent ignition or other damages to plant and people around caused by heat radiation and possible dropout of burning liquid. Also any releases of flammable vapour from other parts of the site should disperse to below their lower flammable limit before reaching the flare.

Cooling towers have large spacings around them. If the release of flammable materials into the cooling water and then into the atmosphere is possible, there must not be any ignition sources near the tower. Cooling towers produce large volumes of wet air, which can cause problems of fog, precipitation, freezing and corrosion in areas downwind of them. Cooling towers also require water basins and substantial foundations.

Other utility systems have quite wide spacing recommendations too: Boilers have flame and hot surfaces, which can act as ignition sources. Large distances are often recommended for compressors to separate possible leaks from ignition sources. Compressors may cause a considerable amount of vibration, which may cause leaks in piping. They also need clear space around them to be maintained and operated properly.

Storage vessels are usually located on tank farms. The space around a tank and the distances to other equipment depend on the materials stored, their potential hazardousness and the possibility of the unexpected changes in storage conditions. Fluid storages should be in a safe location away from process and public areas. It is also important to prevent fire spreading between tanks by keeping the level of heat radiation in an acceptable level (Mecklenburgh, 1985).

Process industry needs different types of vessels for storing their products and raw materials. Storage vessels may be atmospheric or pressurised, fixed or floating roof tanks, or low or high temperature tanks according to the material stored. The safety aspects of different storage tanks are affected by the phase of fluid (gas/liquid), storage pressure and flash points of stored substances. Therefore the spacing recommendations are given for each vessel type separately (see Table 19). Pumps may also handle fluids below or above their flash or autoignition points. This is recognized by general layout recommendations too.

Table 19. Comparison of the average spacing recommendations for some OSBL items.

Equipment items	Average equipment spacing in metres by		
	Bausbacher and Hunt (1993)	Prugh (1982)	Mecklenburgh (1985)
Flare on ground, open on ground, schielded	60–120 120 120	 150 95	>60
Cooling towers	78	49	31
Boilers /boiler houses	75	41	
Compressors	59		48
Blowdown facilities	75	43	
Pressure storage tanks	74	49	35
Low pressure gas storage tanks (< 1 bar g)	74		34
Atmospheric flammable liquid storage tanks (FP<38°C)	72	43	34
Atmospheric storage tanks (FP>38°C)	72	40	
Pumps above autoignition		34	
Pumps (light ends and other flammables)		30	
Pumps handling non-flammables		24	

11.4.3 Equipment Involved in Large Losses

Mahoney (1997) has analysed the 170 largest losses in refineries, petrochemical plants and gas processing plants from 1966 to 1996. Nearly all the losses in the analysis involved fires or explosions. Most common primary cause of losses was piping. Instone (1989) analysed some 2000 large loss claims of hydrocarbon industry at Cigna Insurance. Table 20 lists the ISBL equipment and Table 21 lists the data of the OSBL equipment by Mahoney (1992, 1997) and Instone (1989).

Table 20. Some ISBL equipment involved in large losses.

Types of equipment	Percent of Losses (%) (Mahoney, 1992)	Average Dollar Loss (Millions $) (Mahoney, 1992)	Proportion of Losses (%) (Instone, 1989)
Reactors	13	67.9	3
Process drums	7	26.1	3
Pumps – compressors	6	29.1	5+5
Heat exchangers	4	23.8	4
Process towers	4	58.5	3
Heaters - boilers	2	18.6	10+5

In Table 20 reactors were involved in 13% of incidents (Mahoney, 1992) and produced the highest average loss, because an explosion-damaged reactor spreads devastation to a large area. On the other hand process towers were involved in only 4% of incidents, but they produced the second highest average loss. Few accidents were caused by process towers but great economical losses were due to the large inventories involved, which lead to expensive consequences in the nearby process units. Heaters and boilers caused only 2% of incidents and they had the lowest average loss. In many cases it is however probable that heaters and boilers have been the secondary causes of failure as an ignition source, which is not taken into account in Mahoney's data.

By Instone (1989) process unit types most often involved in large losses seem to be furnaces or boilers (15%), whereas reactor or process drums seem to be quite rarely involved (3% each). These are the major differences between Mahoney's and Instone's data (Table 20). A possible reason for the differences is that Instone has analysed the process units *involved* in large losses and Mahoney has analysed the *primary causes* of large losses.

Table 21. Some OSBL equipment involved in large losses.

Types of equipment	**Percent of Losses (%) (Mahoney, 1997)**	**Average Dollar Loss (Millions $) (Mahoney, 1997)**	**Proportion of Losses (%) (Instone, 1989)**
Tanks	15	62	14
Pumps – compressors *	8	68	5+5
Heaters - boilers *	2	16	10+5
Warehouse			3
Flare			<1
Cooling tower			<1
API separator			<1

* include both OSBL and ISBL

In Mahoney's data (1997) for OSBL tanks in general have been involved in 15% of accidents. Large inventories and high replacement costs of tanks with their assessories lead to expensive consequences as can be seen from the average loss column in Table 21. Pumps and compressors were involved in 8% of incidents, but they produced the highest average loss. This is due to high replacement costs of compressors and their electrical installations. Pumps are often located nearby each other. Therefore an accident destroys several pumps with their electrifications at the same time. Heaters and boilers were involved only in 2% of incidents and they had the lowest average loss.

In Instone's data (1989) the OSBL equipment most often involved in large losses seems to be storage tanks (14%). Heaters and furnaces are mentioned in 15% of incidents. Pumps, compressors and boilers are involved equally (5% each) in large losses, whereas flares, cooling towers and API separators happen to be quite rarely involved (<1% each).

There are distinct differences between Mahoney's and Instone's data (Table 21) concerning fired heaters and boilers. A possible reason for this is that Instone has analysed the process units involved in large losses and Mahoney has analysed the primary causes of large losses. It is known that heaters and boilers are the most common ignition sources (see Table 22) and therefore probably considered as secondary causes by Mahoney.

Table 22. Some sources of ignition.

Ignition sources	**% of ignitions (Instone, 1989)**	**% of known ignitions (Planas-Cuchi et al., 1997)**	**% of known ignitions (Fire Protection Association, 1974)**
Hot surfaces	18	16	18
Furnace	18	4	
Boiler	<3	2	18
Flare	<3	6,5	

11.4.4 Equipment in Other Indices

A frequently used safety index in process industry is for instance the Dow Fire & Explosion Hazard Index (1987). The Dow F&E Index gives penalties for fired equipment and certain specified rotating equipment. These are a part of the Special Process Hazards, within which the penalties of a process unit are summed.

Fired equipment will have penalties, if the material in process unit near the air intake of fired heater could be released above its boiling point, if the material is a combustible dust, or if the material could be released above its boiling point. The penalty depends on the distance from the possible leak source and it varies between 0.1 and 1.0. For instance the distance of 15 m gives the penalties 0.27 (above the flash point) and 0.60 (above the boiling point). Any situation involving a material processed below its flash point receives no penalty.

Large rotating equipment such as 1) compressors in excess of 450 kW, 2) pumps in excess of 56 kW, 3) agitators and circulating pumps, in which failure could produce a process exotherm, and 4) other large, high speed rotating equipment with a significant loss history, e.g. centrifuges have all a constant penalty of 0.5.

It was noticed that the scale of penalties is much narrower than the scale of recommended layout spacings or the cost of large losses. This is because the Dow F&E Index takes into account only large rotating equipment, which is known more likely to contribute to accidents than smaller equipment. Thus the smaller equipment is safer and it is not given penalties.

11.4.5 Equipment Failures and Their Evaluation

There is a certain amount of statistical information available on the failures of process system components.

Arulanantham and Lees (1981) have studied pressure vessel failures in process plants such as olefins plants. They define failure as a condition in which a crack, leak or other defect has developed in the equipment to the extent that repair or replacement is required, a definition which includes some of the potentially dangerous as well as all catastrophic failures. In olefins plants fired heaters have failure rates of about 0.4 failures/year, while process pressure vessels have 0.0025 failures/year and heat exchangers 0.0015 failures/year. It is noticed that fired heaters are much unsafer than process pressure vessels, which are a little unsafer than heat exchangers.

In the Canvey study (King, 1990; Health and Safety Executive, 1978) the potential hazards to the public from the industrial activities in the Canvey Island/Thurrock area of Essex was studied. The study showed that pressure vessels had ten times bigger assumed frequency of catastrophic failures than LPG-pumps.

Crawley and Grant (1997) have developed a risk assessment tool for new offshore installations. They have examined typical leak frequencies of equipment items and the ignition probability of these leaks in four pressure bands. With this information it was possible to define leak size and frequency for any piece of equipment and the ignited leak frequency. In off-shore installations gas separation vessels were found to have ten times higher ignited event frequency than oil pumps.

11.4.6 Equipment Safety Subindex for ISBL

For the generation of the equipment safety subindex the data discussed in the previous chapters were evaluated:

It was noticed that the order of process items in the layout spacing recommendations is almost identical. The furnaces and fired heaters are on the top of the list (see Table 18). The next group is formed by compressors and high hazard reactors. Air coolers, ordinary reactors and high hazard pumps appear next. After that come towers, process drums, heat exchangers and pumps. The last and safest group is formed of equipment handling nonflammable and nontoxic materials.

The only discrepancy in the layout recommendations is the higher ranking of towers and drums in the Industrial Risk Insurers (1991) data. The higher ranking for vessels is probably because of the large inventory of flammables in such vessels, which causes an added danger. Since the inventory is considered separately by the inventory subindex in the ISI, the vessels may best be included into the same group as heat exchangers and pumps.

Accident statistics on the equipment involved in large losses give somewhat contradictory information (see Table 20). According to Mahoney (1992) the most common process items as primary accident cause are reactors. The next in the list are process drums whereas heaters are one of the safest. This contrasts with Instone's (1989) data, where heaters and boilers were the most common process items in the accidents, whereas reactors and process drums were quite uncommonly involved. This difference may be partly because Mahoney has analyzed the primary causes of large losses, whereas Instone has listed the involvement of equipment in losses. Since furnaces are sources of ignition for flammable leaks from other equipment, furnaces are not necessarily listed as primary causes even they are probably involved as secondary causes in many losses. Therefore the inclusion of both reactors and furnaces in the list of most unsafe equipment is well justified.

We have ranked furnaces unsafer (score 4) than reactors (score 3 or 2), since fired heaters are the most common ignition sources (Instone, 1998) for any leaks. Instone (1989) also lists furnaces as the most commonly involved process items in losses. This is also confirmed partly by Dow Fire and Explosion Index (1987), which can give higher penalties for furnaces than for reactors (i.e. cooling systems and agitators of reactors) or large compressors. Also Arulanantham and Lees (1981) give very high mechanical failure rates to olefin plant fired heaters.

Compressors are ranked very unsafe because they are referred as very vulnerable process items (Marshall, 1987), since they contain moving parts, they are subject to vibration and they can release flammable gas in a case of failure. Compressors are also very high in the layout list.

For process drums, towers, heat exchangers and pumps Mahoney (1997) and Instone (1989) give similar loss statistics, which are low (Table 20). Arulanantham and Lees (1981) give these process items roughly the same mechanical failure rates. From this and the layout data we have concluded that process drums, towers, heat exchangers and pumps (below autoignition) can be grouped together as one single low score level (score 1) in the equipment subindex.

As seen the accident statistics and risk analysis data confirms to large extent the information from layout safety distances. To summarize; the process items were arranged into five groups; the safest group is the equipment handling nontoxic and nonflammable material, the second group contains common process items such as process drums, pumps and heat exchangers, third group hazardous equipment such as reactors and pumps above autoignition, fourth group more hazardous items such as high hazard reactors and the most unsafe group is the equipment containing ignition sources such as fired heaters. Full compilation of equipment ranking for ISBL is given as Table 23. Note: "high hazard" refer to process items handling materials above their autoignition point.

Table 23. The scores of Equipment Safety Subindex I_{EQ} for ISBL.

Equipment items	**Score of I_{EQ}**
Equipment handling nonflammable, nontoxic materials	0
Heat exchangers, pumps, towers, drums	1
Air coolers, reactors, high hazard pumps	2
Compressors, high hazard reactors	3
Furnaces, fired heaters	4

11.4.7 Equipment Safety Subindex for OSBL

For offsite equipment the scores 0–3 have been used instead of scores 0–4 for ISBL equipment (Heikkilä and Hurme, 1998b), since the offsites represent only one third of all losses (Instone, 1989) and are therefore not as essential as ISBL. Also much of the risks of OSBL are due to the large inventory of flammable or toxic chemicals, which are discussed by the inventory, flammability and toxicity indices, not by the Equipment Safety Index. Also the equipment of same size is probably safer in OSBL than in ISBL because of the larger spacings in layout.

The order of process items in the layout spacing recommendations (Table 19) is quite similar. The flares are on the top of the list. The next unsafe are cooling towers, boilers and compressors. Storage tanks under pressure appear next. After that come low pressure and atmospheric storage tanks and pumps of flammable liquids. The last and safest group is formed of equipment handling nonflammable and nontoxic materials.

Accident statistics on the equipment involved in large losses (Table 21) give somewhat contradictory information. According to Mahoney (1997) the most common process items as primary accident cause within offsite systems are tanks. Fired heaters and boilers represent only 2% of losses, while in layout they are recommended about the same spacings as tanks (Table 19). Mahoney's data is quite similar with Instone's (1989) data, except Instone has much larger loss rates for heaters and boilers. This difference may be partly because Instone discusses only hydrocarbon processing plants, while Mahoney has studied hydrocarbon, chemical and petrochemical plants. Also Mahoney has analysed the primary causes of large losses, whereas Instone has listed the involvement of equipment in losses. Since heaters and boilers are very common sources of ignition (Table 22) for flammable leaks from other equipment, they are not necessarily listed by Mahoney even they are probably involved as secondary causes in many losses. Therefore the inclusion of heaters and boilers in the list of most unsafe equipment is well justified.

Flares are not high in the lists of Mahoney (1997) and Instone (1989). However Planas-Cuchi et al. (1997) list them equally important as furnaces and boilers together as ignition sources (Table 22). From this it has been concluded that flares should be included in the same equipment hazard group with boilers and furnaces in the Equipment Safety Index for OSBL. Therefore all equipment which act as sources of ignition through flame such as furnaces, boilers and flares were considered the most dangerous equipment and given the score 3 due to high loss statistics (Instone, 1989, Table 21) and their function as sources of ignition (Table 22).

Into the next index group (score 2) it was located high and low ($p< 1$ bar g) pressure tanks, refrigerated storage tanks, compressors, and cooling towers which all represent a source of flammable gas. They are located also high in the lists of layout spacings (Table 19) and in the lists of large losses (Table 21).

Atmospheric storage tanks of flammable liquids and pumps of flammable or toxic liquids are located in the equipment safety group 1, since they are sources of flammable liquid which do not produce a vapour cloud directly.

Equipment handling nonflammable and nontoxic material belong to the safest group (score 0). See Table 24 for the list of scores.

To summarize the safest equipment is handling nontoxic and nonflammable materials. The second safety group includes systems with flammable liquids such as atmospheric storage tanks and pumps. The third group contains possible sources of flammable gas such as cooling towers, compressors and pressurised storage tanks. The fourth group contains the most unsafe offsite items which act as ignition sources such as flares, boilers and furnaces.

Table 24. The scores of Equipment Safety Index I_{EQ} for OSBL.

Equipment items	Score of I_{EQ}
Equipment handling nonflammable, nontoxic materials	0
Atmospheric storage tanks, pumps	1
Cooling towers, compressors, blowdown systems, pressurised or refrigerated storage tanks	2
Flares, boilers, furnaces	3

11.5 Safe Process Structure Subindex

A process structure defines which operations are involved in the process and how they are connected together. Therefore the Safe Process Structure Subindex describes the safety of the process from system engineering point of view. It describes: how well certain unit operations or other process items work together, how they should be connected and controlled together. The index describes also how auxiliary systems such as cooling, heating or relief systems should be configured and connected to the main process. The importance of this subindex is increasing as the processes are becoming more integrated through heat and mass-transfer networks. (Heikkilä et al., 1998)

The Process Structure Subindex does not describe the safety of process items as such or their interaction through nonprocess route (i.e. through layout), since this is described by the Equipment Safety Subindex (Ch. 11.4).

11.5.1 Evaluation of Safe Process Structure

Many different alternative process configurations can be created for a process in the conceptual design phase. In choosing the most feasible alternative safety should be one of the major evaluation criterias. Therefore information on the safety features of alternative process structures are needed on preliminary process design.

Most of the subindices of ISI are quite straightforward to estimate since they are e.g. based on the physical and chemical properties of compounds present. The process structure subindex looks at the process from a systems engineering point of view. Therefore it is much more difficult to estimate. In fact there is no explicit way of estimating the safety of the process structure but one has to rely on experience based data which is documented as standards, design recommendations and accident reports.

11.5.2 Sources of Experience Based Safety Information

Process solutions have shown their strong and weak, safe and unsafe points in operation practice. The knowledge of practising solutions consists of the details collected during the operation and maintenance. Practising solutions reveal for instance which unit operations are preferable for certain purposes and how the units can be connected safely together. Some of the information can also be found from design standards which have been created on the basis of the experience on the operation of existing process plants (Lees, 1996).

Another source of design information is the accident reports made after an accident. They give valuable information of the possible weaknesses that can occur in unit operations, while they are used for certain purposes. In the past many of the unit operations have shown their adverse characteristics. This information is mainly collected to accident reports and included to safety standards. Accident reports tell us for example:

- which process equipment configurations have unfavourable properties
- which type of chemicals do not suit to certain unit operations
- which unit operations/ configurations are risky
- when the connection of process units should be avoided.

The difficulty in utilizing accident reports lies in the lack of accident report standards. Reports vary a lot how they document the details of the accident itself, the path to the final event, the causes, and the consequences. Still the reports can tell much experience based information which can - and should be - utilized in designing new plants. In fact a major goal in improving the design of safe process plants should be to enhance the reuse of design experience. This is important since the same mistakes are done again and again (Kletz, 1991).

A more refined form of accident reports is an accident database, where all the reports are presented in a standardized format. Extensive databanks have already been collected from accident reports (Anon, 1996). This kind of standardized format allows easier retrieval of accident information also by computerized means.

11.5.3 Structure of the Database

The basis for the estimation of safe process structure lies in the integration of the two types information sources: 1) recommendations and standards how the process should be designed, and 2) accident database which describes the negative cases from which one can learn. Therefore a casebase of good and bad design cases is needed. Both of these information sources should be readily available to the design engineer through the database. A design problem can be compared with the cases in this combined databank for instance by case-based reasoning.

In this approach accident cases and design recommendations can be analysed level by level. In the database the knowledge of known processes is divided into categories of process, subprocess, system, subsystem, equipment and detail (Fig. 6). Process is an independent processing unit (e.g. hydrogenation unit). Subprocess is an independent part of a process such as reactor or separation section. System is an independent part of a subprocess such as a distillation column with its all auxiliary systems. Subsystem is a functional part of a system such as a reactor heat recovery system or a column overhead system including their control systems. Equipment is an unit operation or an unit process such as a heat exchanger, a reactor or a distillation column. Detail is an item in a pipe or a piece of equipment (e.g. a tray in a column, a control valve in a pipe).

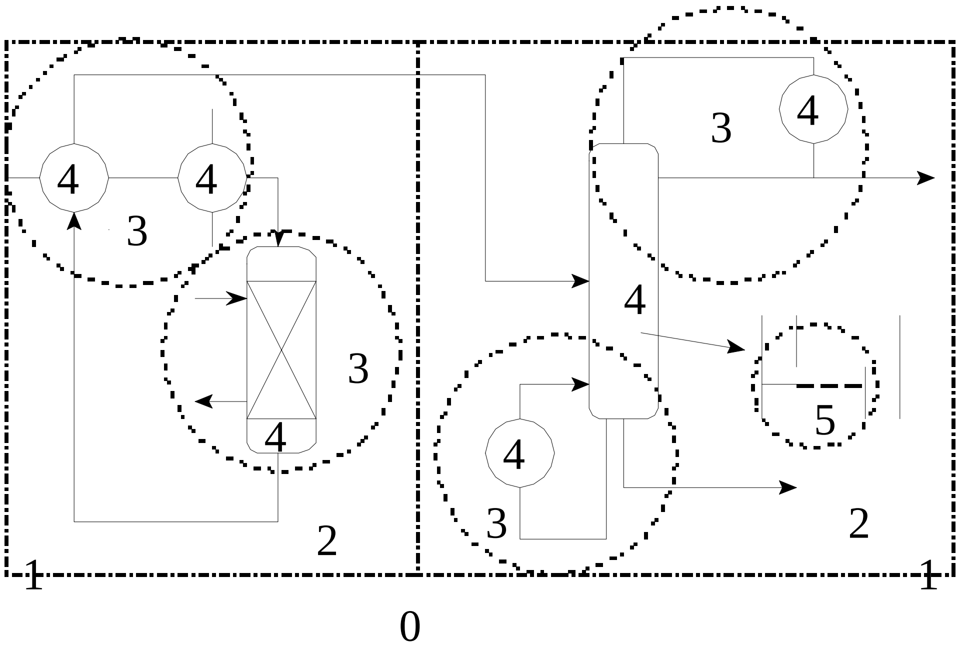

Figure 6. Example of the levels of the process as used in the CBR database. (0 = process, 1 = subprocess, 2 = system, 3 = subsystem, 4 = equipment, 5 = detail).

A search for cases in the databank can be made on these levels on the basis of the nature of the design problem. If a process is being designed from beginning the first search is made for a whole process. The search is then made for those subprocesses, systems, subsystems and equipment, which are informable for the design. On the basis of the retrieved information the designer can evaluate the right index value for the process structure of the section under review. The input data for a database search contains information on the process level and on the raw materials and products, reaction types and their details such as catalysts and phase of reaction. As output there is information about the unfavourable process configurations, recommended configurations and accident cases.

A plant is divided into inside and offsite battery limit areas. The configurations of ISBL and OSBL areas differ considerably. Generally the size of equipment, the amount of chemicals and also the spacings are larger in OSBL area. The safety of the process structure is also affected by these factors. Therefore this aspect is included also into the database.

The database does not always contain information which is directly related to the process under review. Therefore it is important to be able to use analogies. In general much of the design of new processes relies on analogies. For example most hydrogenation processes have similar features, most tanks of liquefied gases have similarities etc. For that reason information has been included into the database on the type of materials in incident (e.g. liquefied gas), the type of the reaction (e.g. oxidation), the thermal nature of the reactor (e.g. exothermic), the phase of the reaction and the type of catalyst.

To learn from the accident cases it is essential to indicate the type of incident which happened (e.g. explosion), the direct cause of the incident (e.g. static electricity), the reason why this could take place (e.g. filling through the gas phase) and finally - most important - the lesson how this can be avoided (e.g. fill the tank through the bottom).

11.5.4 Inherent Safety Index of Safe Process Structure

Process structures are divided into six groups of scores from 0 to 5 according to the knowledge of their safety behaviour in operation. The first group is the safest group with the score 0. It consists of recommended and standardized process and equipment solutions. The second group is based on sound engineering practice, which implies the use of well known and reliable process alternatives. In the third group there are processes which look neutral, or on which there is no safety data available. The fourth group includes configurations which are probably questionable on the basis of safety even accidents have not occured yet. The fifth and sixth groups contain process cases on which documented minor or major accident cases exist respectively. The final score of the subindex is chosen on the basis of the worst case of different levels of the reasoning. The results can be used with other subindices for estimating the total inherent safety of process alternatives for the selection of process concept or details of the process configuration. Details of the Safe Process Structure Subindex are given by Heikkilä et al. (1998).

Table 25. Values of the Safe Process Structure Subindex I_{ST}.

Safety level of process structure	**Score of I_{ST}**
Recommended (safety etc. standard)	0
Sound engineering practice	1
No data or neutral	2
Probably unsafe	3
Minor accidents	4
Major accidents	5

12. Case Study

As a case study an acetic acid process has been given. Acetic acid is produced by a liquid-phase methanol carbonylation. Acetic acid is formed by the reaction between methanol and carbon monoxide which is catalysed by rhodium iodocarbonyl catalyst. The process diagram is shown in Figure 7.

The methanol carbonylation reaction is carried out in the reactor (1) at about 175°C and 30 bar. Gases from the reactor (1) are led to the separator (2) where condensables are separated from the carbon monoxide and inerts. The gas phase is then led to the scrubber (3) where organics are removed by using methanol. Effluent stream of the separator (2) is recycled to the reactor with the methanol stream from the scrubber (3). Liquid from the reactor (1) is led to the distillation column (4) for the separation of light and heavy ends, which both are recycled back to the reactor (1). The acetic acid side-draw from the light ends separator (4) is led to the drying column (5) for water removal. The bottoms of the drying column (5) containing dry acetic acid are led to the product column (6) where any heavy by-products are removed. The acetic acid overhead is then led to the finishing column (7) for final purification.

The chemical substances in the process are all flammable and /or toxic in varying degrees. The process streams pose different hazards according to the type and quantity of chemicals present. The capacity of process is 100000 t/a acetic acid.

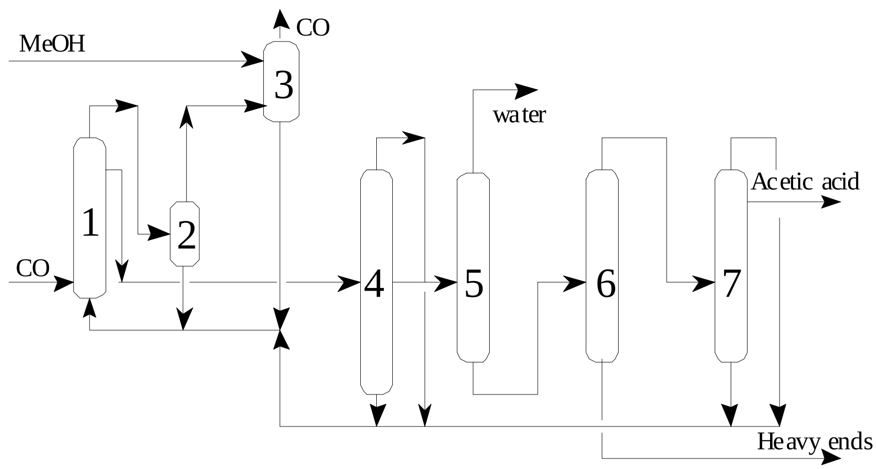

Figure 7. Flowsheet of the acetic acid process: 1) reactor, 2) separator, 3) scrubber, 4) light ends separator, 5) drying column, 6) product recovery, 7) product finishing.

For the safety comparison analysis the ISBL of acetic acid process was divided into two steps: reaction section (reactor, separator, scrubber) and distillation train. Both steps were handled separately during the analysis. The analysis of the data and the results are presented in the Table 26 for reaction section and in the Table 27 for the distillation train.

The heats of main and side reactions are calculated by Equation 6 for the whole liquid inventory. For the main reaction the heat is about 300 J/g. The formation of propionic acid gives the maximum heat of side reaction which is about 1000 J/g. The most dangerous chemical in this process is carbon monoxide which appears in the reaction section. As a construction material stainless steel and Hastelloy are both needed. Hastelloy gives the score value 2. Most dangerous chemical interaction may appear between methanol and hydriodic acid in the reaction section resulting heat formation and even a fire, which gives the score 4.

The inventory in the process is 100 tonnes when all seven vessels have been calculated together with one hour residence time. The maximum process temperature is 175°C in the reactor. The highest process pressure is 30 bar in the reaction section. The equipment safety is determined by the CO feed-gas compressor (score 3). Ordinary reactor gives score 2 and a high hazard reactor score 3 (Table 23).

The Safe Process Structure Subindex for the acetic acid process is discussed in more detail in Chapter 13.2.

Table 26. Safety analysis for the reaction section of the acetic acid process.

Reaction section			**Score**
Chemical inherent safety index			
Heat of main reaction	~ 300 J/g		1
Heat of side reaction, max	~ 1000 J/g		2
Flammability, Explosiveness, Toxicity	Maximum sum for CO		10
Corrosiveness	Stainless steel / Hastelloy		2
Chemical interaction	worst interaction: methanol - hydriodic acid		4
		Σ	19
Process inherent safety index			
Inventory	100 t/h		3
Process temperature, max	175 °C		2
Process pressure, max	30 bar		2
Safety of equipment	feed-gas compressor		3
		Σ	10
Total inherent safety index			**29**

The total inherent safety index for reaction section is higher than for distillation train. Consequently the distillation train is inherently safer than the reaction section since:

- In the distillation train there are no potential reactions, except potential interaction.
- Most dangerous chemical is carbon monoxide which appears only in the reaction section.
- The process pressure is higher in the reaction section.

- The equipment safety is worse in the reaction section due to the feed-gas compressor and the reactor.

Table 27. Safety analysis for the distillation train of the acetic acid process.

Distillation train			**Score**
Chemical inherent safety index			
Heat of main reaction	no reaction		0
Heat of side reaction, max	no side reactions		0
Flammability, Explosiveness, Toxicity	Maximum sum for acetic acid		7
Corrosiveness	Stainless steel / Hastelloy		2
Chemical interaction	worst interaction: methyl iodide – hydriodic acid		4
		Σ	13
Process inherent safety index			
Inventory	100 t/h		3
Process temperature, max	155 °C		2
Process pressure, max	4 bar		0
Safety of equipment	Distillation tower		1
		Σ	6
Total inherent safety index			**19**

13. Case-Based Reasoning for Safety Evaluation

When problem solving is based on experience which is difficult to define as explicit rules, it is possible to apply case-based reasoning (CBR). CBR uses directly solutions of old problems to solve new problems. The functional steps in CBR are (Gonzalez and Dankel, 1993):

1. New problem presentation.

2. Retrieval of the most similar cases from case-base.

3. Adaptation of the most similar solutions for generating a solution for a current problem.

4. Validation of the current solution.

5. Learning from the problem cases by adding the verified solution into the case-base.

A data table of a case-base can be divided into input and output sections. Input parameters are retrieval parameters and output parameters are design specification parameters. The problem is characterized as input data to the system. In the retrieval phase a set of retrieval parameter values of all cases in the case-base are compared to the input data. The most similar cases are then selected and ranked based on the comparison.

In the case of string data types suitability is simply:

$$X_i = C_{i,j} \Rightarrow Y_{i,j} = 1 \quad (7)$$

$$X_i \neq C_{i,j} \Rightarrow Y_{i,j} = 0 \quad (8)$$

where X_i is the input value of parameter i, $C_{i,j}$ is the value of parameter i of case j, and $Y_{i,j}$ is the suitability of a parameter i for the case j.

The quality of reasoning increases, if the importance of selection parameters can be altered. The user should determine the importances of selection parameters for the topic under study. Weighted suitability R_{ij} can be expressed:

$$R_{ij} = W_i Y_{i,j} \tag{9}$$

where W_i is weight factor of a selection parameter i evaluted by user. Overall suitability can be calculated for the case j based on the number of parameters N and parametric suitabilities R_{ij}:

$$S_j = \frac{\sum_{i=1}^{N} R_{i,j}}{N} \tag{10}$$

Case-based reasoning has earlier been used for instance for equipment design. Koiranen and Hurme (1997) have used case-based reasoning for fluid mixer design and for the selection of shell-and-tube heat exchangers. They have included an estimation of design quality for the case retrieval beside technical factors.

Chung and Jefferson (1997) have combined the IChemE Accident Database (Smith et al., 1997) with case-based reasoning to create an automatic data retrieval for designers' and operators' use. They intend to develop an intelligent system, which takes for example the term 'electrical equipment failure', works out all the related terms and retrieves the relevant information automatically. The method should be integrated with computer tools used by designers, operators and maintenance engineers so that appropriate accident reports can be automatically presented to the user. The employed IChemE database contains much information on accident causes. The aim of the system presented by Chung and Jefferson (1997) is to find all relevant causes of past accidents to improve processes, whereas our CBR system is intended for reasoning on the structure of a process and its favourable and unfavourable characteristics for preliminary process design purposes. The database used by Chung and Jefferson (1997) is an accident database, whereas our database contains also design recommendations. On the other hand our CBR system is intended specifically for the use of process designers, but the system of Chung and Jefferson (1997) is developed for wider use from chemical plant designers and operators to maintenance teams.

13.1 Description of Prototype Application

Prototype CBR application has been implemented on MS -Excel spreadsheet. The program has been organized on several sheets. A database of cases was created which consists of accident cases collected from literature (e.g. Lees (1996) and Loss Prevention Bulletin) and of design recommendations. The application program includes retrieval functions which are used to retrieve the most suitable cases from the database.

13.1.1 Input and Output Parameters

The scope of a database search is defined by using categories of process, subprocess, system, subsystem, equipment and detail as input parameters. This hierarchy is used for clarifying the process structure and for making the use of process analogies more feasible in reasoning. E.g. a condenser has certain safety characteristics undependent on the process it is located. Beside the process structures input parameters include the raw materials and products and some reaction details. The importance of the parameters may be evaluated by using weighting factors.

Output parameters contain the input parameters plus information on the safety characteristics of the process and information on accidents and their causes. Specific design recommendations are included in the output. On the accidents the output describes e.g. following information:

- what kind of incidents have happened
- what is the actual cause of the incident
- what are the contributing factors or circumstances of the incident
- how to improve the application for better safety

All stored cases are validated on the basis of the Safe Process Structure Subindex. The validations are given for every case and included in the output. Further information on the cases is given as appendices, which describe the case in more detailed.

13.1.2 Retrieval of Cases

In this work the cases in the database are stored on their own MS-Excel worksheets. The stored cases are copied on a retrieval calculation data sheet during the retrieval phase. All retrieval parameters in this application are textual string parameters. Thus the comparison between casebase and input problem is simple. When the input value is equal with the case value, the distance is 1, otherwise the distance is 0. The weighted suitability of parameters is then calculated by Equation 9. The weighting factors are introduced by the user. Overall suitability is calculated by Equation 10. Cases are ranked according to their overall suitability and the five nearest cases are shown for the user on an output worksheet.

The retrieval of cases can be done in several steps. The first step is the evaluation of the process with the stored cases. This way can be seen, if the process is safer or unsafer than the alternative processes. The second step is the safety evaluation of specific process systems, subsystems or pieces of equipment. The database contains improvement recommendations to avoid the same accidents happening again. The evaluation of processes can be extended to detailed level. Also the equipment details or safety valves etc. can be checked on this level.

13.2 Case Study

For the evaluation of the safe process structure of the acetic acid process (Ch. 12, Fig. 7) CBR database searches were done on two levels (Heikkilä et al., 1998). First level was the acetic acid process as a whole. On the second level the reactor system was studied in more detail.

13.2.1 CBR on Process Level

First the acetic acid process was studied as a whole to find out if the alternative processes have differences in the safety on the conceptual (i.e. process) level. The search (Table 28) found cases for carbonylation and oxidation processes (Table 29). It can be seen that there has been explosions and fires on both types of plants. The explosion in the carbonylation plant was due to static electricity in loading of a storage vessel. This type of explosions are not specific to carbonylation plants, but they are possible also in many other processes. The fires and explosions on the oxidation plants were related to the chemicals present in that process. They are more likely to happen in such a plant than somewhere else. Thus the carbonylation process can be considered safer than the oxidation process based on the information from this search.

Table 28. Input data of the search for the acetic acid process.

INPUT DATA

Retrieval parameters	**Active**	**Importance**	**Value**
raw material	TRUE	9	methanol
product	TRUE	9	acetic acid
reaction type	FALSE		
termic type of reaction	FALSE		
phase of reaction	FALSE		
catalyst	FALSE		
ISBL / OSBL	TRUE	6	isbl
system	FALSE		
subsystem	FALSE		
equipment	FALSE		
detail	FALSE		

Table 29. Output data of the search for the acetic acid process.

	1st Case	2st Case	3st Case
PROCESS:			
Raw material	methanol	butane	butane
Product	acetic acid	acetic acid	acetic acid
Reaction type	carbonylation	oxidation	oxidation
Thermic type of reaction	exo	exo	
Phase of reaction	liquid	liquid	liquid
Catalyst	Rh complex		
Isbl / Osbl	isbl	isbl	isbl
SYSTEM		reaction	reaction
SUBSYSTEM	intermediate storage	purging	feed
EQUIPMENT	tank	reactor	boiler
DETAIL	inlet pipe		
Incident:	explosion	fire	explosion
Cause 1:	static electricity	self-ignition of acetaldehyde	oxygen leak
Cause 2:	filling through vapor phase	methane ignited	
Recommendations:	fill through bottom		
Material:	acetic acid	acetaldehyde	butane/air
Nature of material:	organic acid	aldehyde	LPG
Safety Index (0-5)	4	4	5
Appendix:			App.1

Appendix 1: Explosions occured because pure oxygen entered a gas-fired boiler and mixed with the butane and steam used to form acetic acid. The first blast occured near a gas fired boiler and the second blast occured at a nearby reactor. (3 killed, 37 injured)

13.2.2 CBR on the Reactor System

In the second phase searches were made on the system and subsystem level. This is needed for the comparison of process alternatives and for the design of the exothermic reactor and its heat transfer systems. Carbonylation of methanol is an exothermic reaction. Thus only the exothermal reactors were searched. The CBR search found two cases which are general recommendations on the design of exothermic reactors with heat transfer systems. They are shown in Fig. 8 and 9.

The case in Figure 8 represents a reactor with two different cooling systems. In the not recommended case (right) the cooling system presents a feedback loop between a reactor heat rise and the rise in the coolant temperature, which should be avoided. On the left is the recommended system, where the coolant temperature does not depend on the reactor temperature.

The case in Figure 9 shows a heat recovery system of a reactor. The not recommended case on the left shows the feed to an exothermic reactor being heated by the product. In this case the temperature rise in the reactor may lead to the temperature rise in feed. The recommended case on right is safer since the connection is broken because the heat transfer is done by generating and using medium pressure steam.

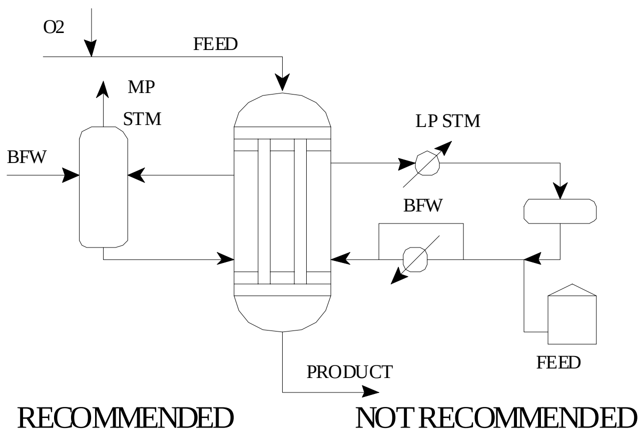

Figure 8. A recommendation to avoid the feedback loop between a reactor heat rise and a rise in coolant temperature.

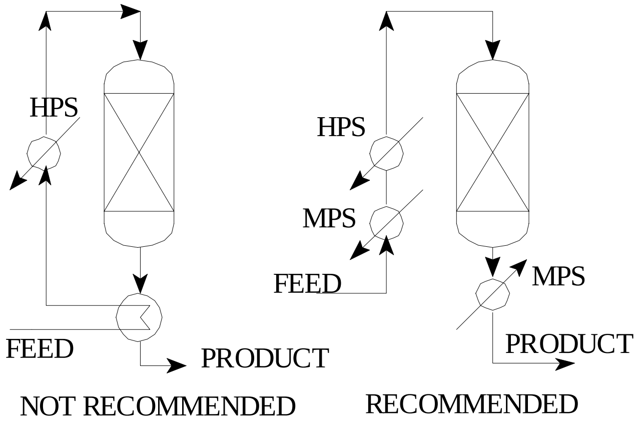

Figure 9. A recommendation for preheating the feed of an exothermic reactor.

13.2.3 Score of the Safe Process Structure Subindex

From the reasoning on the process level we get score 2 (no data or neutral) for the carbonylation process, since the found case was not specific to this process. For oxidation process we get score 5, since a major accident has taken place.

For the recommended reactor system we can get scores 0 (recommended/ standard) or 1 (sound engineering practice) depending how we value these recommendations.

The final score of the Safe Process Structure Subindex for the carbonylation process would be 2 based on this limited reasoning, since the final score of I_{ST} is chosen on the basis of the worst case. Of course in practice one should do the reasoning on all the systems and subsystems in the process. This case study was given only to represent the principle of CBR in reasoning the value of the Safe Process Structure Subindex.

14. Application of Inherent Safety Index for Computerized Process Synthesis

Classically synthesis of chemical processes is based only on economic and engineering aspects. There is however an increasing need to evaluate the safety of processes in the early stage of process design, because of government regulations and for practical engineering reasons. It is much easier to affect the process configuration and inherent safety in the conceptual design phase than in the later phases of process design. Consequently safety aspects should be included in the computerized process synthesis. The presented ISI can be used as a tool in the computerized process synthesis to evaluate synthesized alternatives or as an objective function in synthesis. The existent safety estimation methods (e.g. Dow F&E Index, computerized Hazop) are mostly intended for the more detailed engineering phases or for existing plants and are not directly applicable in their full mode in the conceptual phase since they require detailed information on the process equipment. Other methods such as checklists are not easily changed to a function form to be integrated into other design tools.

Process synthesis is a task of formulating the process configuration for a purpose by defining which operations or equipment are used and how they are connected together. There are two basic approaches for process synthesis: 1) classical process synthesis, analysis and evaluation, and 2) optimization of process structure by using a suitable objective function.

14.1 Classical Process Synthesis

Classical process synthesis consists of the synthesis of the alternatives, their analysis and final evaluation. Hurme and Järveläinen (1995) have presented a combined process synthesis and simulation system consisting of an interactive rule-based system which is used for generating process alternatives (Fig. 10). The process alternatives are simulated, costed and evaluated through profitability analysis. The developed system concept combines process synthesis, simulation and costing with uncertainty estimation.

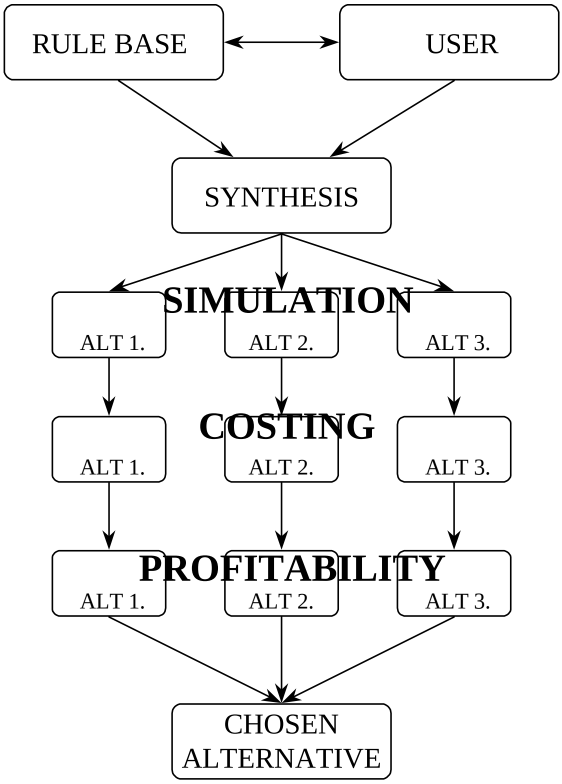

Figure 10. The principle of the approach by Hurme and Järveläinen (1995).

Heikkilä et al. (1996) have expanded the work of Hurme and Järveläinen (1995) with environmental and safety aspects (Fig. 11). The alternatives are simulated to determine the material and heat balances and to estimate the physical properties. Then the alternatives are assessed in economic terms for which the internal rate of return is used. The environmental effects are estimated by equivalent amount of pollutant that takes into consideration the harmfullness of the different effluent substances. With environmental risks are also considered aspects of occupational health to choose inherently healthier process. Even though most health related rules are considered later in the work instructions, health effects should also be a part of the decision procedure. The inherent safety is estimated in terms of the inherent safety index as described later.

The final decision on the best alternative is not a clear choice since the three parameters - cost-efficiency, environmental aspects and inherent safety - cannot be merged into a single figure in a unique way. This is because process designers may emphasize these parameters differently depending on the policy of the company and the goal of the problem in hand. Consequently the alternatives have to be compared based on all the criteria by using for example the decision chart method (Kepner and Tregoe, 1981) or the pairwise comparison matrix presented by Saaty (1977).

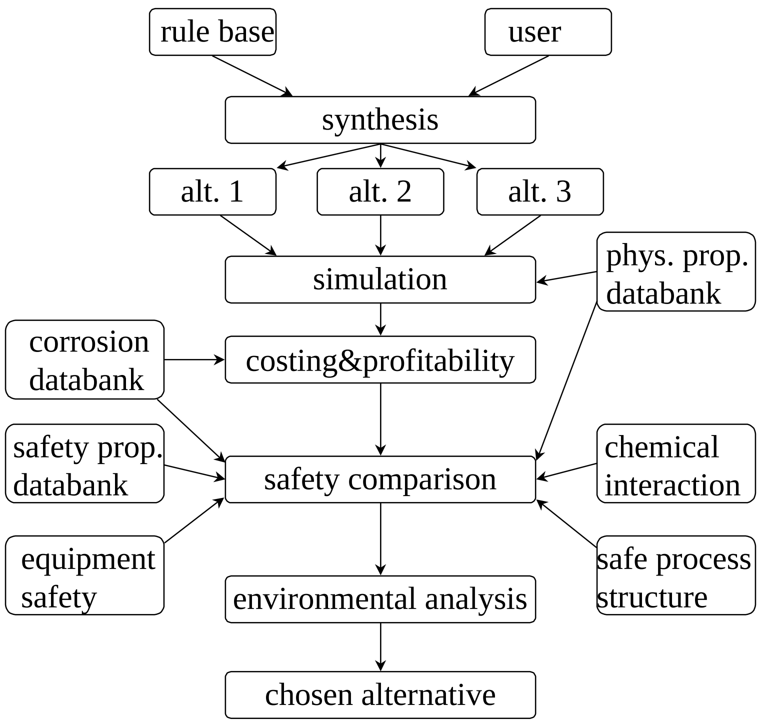

Figure 11. The principles of the combined process synthesis by Heikkilä et al. (1996).

Safety aspects are considered in two phases (Fig. 11). In the rule based synthesis some safety related rules are applied in process concept selections. These include rules such as 'separate corrosive or hazardous components first' or 'avoid using chemically incompatible substances in the same process'.

All safety related matters, such as the selection of raw materials, are not considered in the synthesis phase but are given by the user. Also the generation of universal synthesis rules considering safety is not easy. Therefore it is important to analyze the alternative designs by inherent safety indices which describe e.g. flammability, toxicity, process conditions.

The conceptual design phase is the most critical when designing inherently safer plants, since the alternative process concepts are created and analyzed in this phase. This emphasizes the need to introduce safety evaluation tools into the preliminary process design. Time and money is saved when fewer expensive safety modifications are needed during the later stages of design.

The safety evaluation has to be closely integrated into existing preliminary process design environments to make it readily available during design. The safety tools also benefit from the existing databanks and simulation programs since they can be used for physical property and phase conditions calculations.

The Inherent Safety Index, ISI, was developed to consider a wider range of factors affecting the inherent safety of the process (Ch. 8). The ISI allows the evaluation of inherent safety of process alternatives to be done in a computerized process synthesis environment. The represented synthesis approach allows the inherent safety comparison of process alternatives to be done flexibly and interactively in the conceptual design phase.

14.2 Process Synthesis by Optimization

Process synthesis can be considered as an optimization task. The problem is that the model to be optimized changes at the same time as the process configuration alters. Therefore the possible optimization approaches are MINLP (mixed integer nonlinear programming) and genetic algorithms. MINLP approach has been used in many articles (e.g. Grossmann and Kravanja, 1995). The method is rigorous but requires a dedicated mathematical algorithm. Some of which are still under development.

In the genetic optimization the solution is searched in an evolutionary manner which as such is quite familiar to a practising engineer. The problem here is the requirement of coding the problem as genes and the slowness of the algorithm. This is because many unnecessary cases are calculated due to the mutations and crossovers. The method does not guarantee an optimal solution is reached. GA has already been used for the synthesis of separation process (Hurme, 1996).

14.3 Genetic Optimization

Genetic algorithms (GA) are computational models of natural evolution, which use operations related to genetics to guide an optimizing process in a complex search space. Genetic algorithms work with sets of individuals, which when properly coded, represent potential solutions to the problem. Populations are processed iteratively, starting from a random population, following the phases of evaluation, selection, mating, crossover and mutation (Fig. 12). Selection is based on the evaluation of individuals of a given population by means of a fitness function. The processing cycle is repeated until a termination condition, such as an error tolerance is reached. It is the characteristic of GA that individuals characterized by a common feature and exhibiting a high fitness will have an exponential growth. Even the convergence in not always guaranteed, GAs have been successful in solving difficult optimization problems. GAs do not pose special requirements on the problem to be solved (such as continuity) except that a proper coding of individuals and the existence of appropriate objective function to evaluate the fitness of each individual has to be possible. The proper choice of fitness function is important since it guides the selection and optimization procedure (Goldberg, 1989).

Hurme (1996) has used GA to solve the synthesis problem of the separation of mixture of hydrocarbons. He also compared GA with a pure random version in which the crossover and mutation operations were replaced by a procedure of random generation of new solutions. There was no difference during the first generations but it became significant after some generations. In this case GA reached the solution after ten generations with about 1100 different possible solutions, while the random version required tens of generations. GA seems to be both fast compared to random optimization and not too computationally intensive.

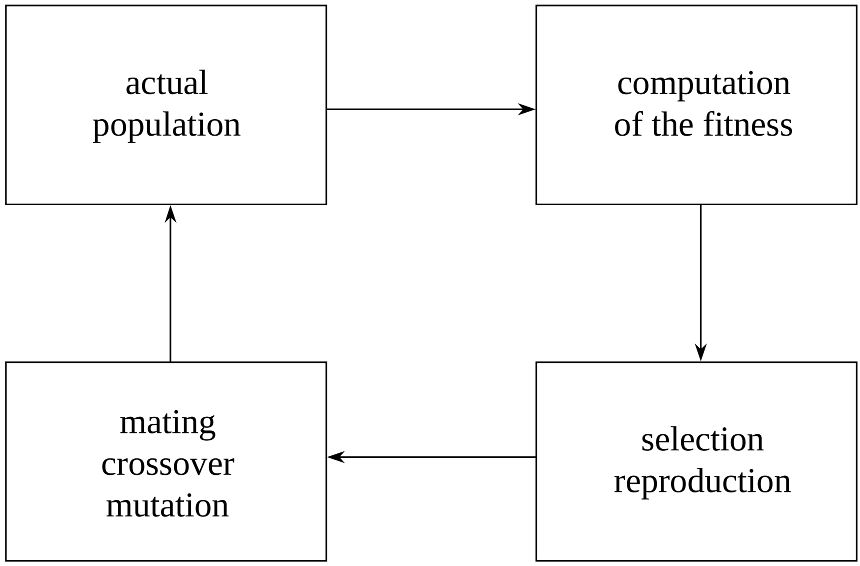

Figure 12. The structure of a classical GA by Moraga and Bexten (1997).

Hurme and Heikkilä (1998) have expanded the GA approach by Hurme (1996) with safety function. Because the model is uncontinuous, ordinary optimization methods cannot be used, but a genetic algorithm is employed instead. In a genetic algorithm the structure of the process is represented as a string of integers, which describes the operations required and how they are connected together. An inherent safety index is used as an objective function in the genetic algorithm (i.e. fitness). The index has been developed for safety estimations in the early stages of process design. Most of the subindices of the method are quite simple to estimate, except the subindex for safe process structure, which is estimated by case-based reasoning by using a database of good and bad design cases. This index can also be used as an objective function to be optimized, if the inherent process safety is to be maximized in a systematic way.

14.4 Principle of the Method

In the approach by Hurme and Heikkilä (1998) inherent safety is the only objective function considered in the process synthesis. It is estimated by the Inherent Safety Index (Heikkilä et al., 1996) which has been developed for inherent safety estimations in conceptual process design. In the synthesis the inherent safety is maximized by using a genetic algorithm. The Inherent Safety Index is used an objective function. The structure of process is represented as a string of integers (gene) representing the required operations, their types and how they are connected. The inherent safety index is the fitness function.

The basic steps of the genetic optimization algorithm are the following:

1) Generation of an initial population of random separation sequences is done first. The sequences describe both which equipment items are used and how they are connected.

2) Random selection of sequences and generation of new solutions using a crossover procedure. The location of crossover in the sequences is also chosen randomly. Since the crossover may result to an impossible sequence, a checking and revision procedure is required. The type of this procedure depends on the type of process synthesized.

3) Mutation of sequences on a randomly chosen location.

4) Evaluation of sequences by using the inherent safety fitness function.

5) Selection of the best sequences and removal of worst and redundant sequences so that the size of population stays constant.

6) Repetition of the steps 2–6 till the change of improvement taking place is below the tolerance given.

14.4.1 Case Study; Separation Process

A synthesis problem on purification of butenes is discussed (Hurme and Heikkilä, 1998). The aim is to synthesize the separation process by maximizing the inherent safety. The inherent safety is measured as the Inherent Safety Index.

In the process a mixture of propane, 1-butene, n-butane, 2-butenes and n-pentane is separated to produce technically pure component streams. Both ordinary distillation (method 1) and extractive distillations (methods 2 and 3) are used.

The feed composition and relative volatilities of adjacent components by using different separation methods are given in Table 30.

Table 30. Feed compositions and relative volatilities in the case study.

Adjacent relative volatilities				
component	**mol-%**	α_1	α_2	α_3
propane	1.47			
1-butene	14.75	2.45	2.0	2.35
n-butane	50.29	1.18	1.17	1.25
2-butenes	27.58	1.03	1.70	1.35
n-pentane	5.90	2.50	2.1	3.0

The separation synthesis problems are of highly combinatorial nature when the number of components and separation methods is large. In this simple five component and three separation methods case there are 1134 different solutions (Hurme, 1996). Two of them are shown in Figure 13 as an example.

The column vapor loads (i.e. vapor flow rates up the columns) are calculated to determine the approximate equipment sizes. An approximate method for calculating the vapor flow V in a column is (Hurme, 1996).

$$V = D\left[1 + \frac{R_F}{(\alpha - 1)}\frac{F}{D}\right] \qquad (11)$$

where $R_F = R / R_{min}$, V is vapor flow, D is distillate flow rate, F is feed flow rate, α is relative volatility, R is reflux rate, R_{min} is minimum reflux rate.

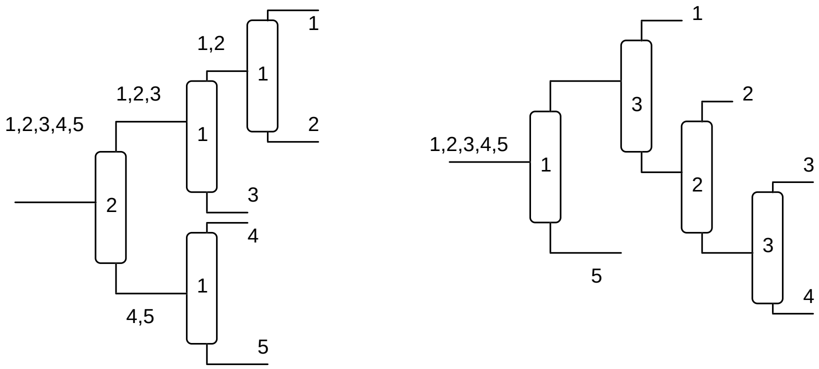

Figure 13. Two process configurations for separating five components 1–5 by three methods 1–3.

The steps of the genetic algorithm are the following:

1) The generation of an initial population of random separation sequences is done first. The sequences describe both in which order the components are separated and which separation method is used. For example the sequence on left in Figure 13 is described by the string 23 12 14 11. The first integer is for the separation method and the second for the heavy key component of the split in the column. The first separation is made by method 2 and the components heavier than no.3 (i.e. 4 and 5) go to bottom. In the next separation method 1 is used and component heavier than 2 (i.e. 3) goes to bottom, etc.

2) Random selection of sequences and generation of new solutions using a crossover procedure is done next. The location of crossover in the sequences is also randomly chosen. The length of crossover is fixed to two components. Since the crossover may result to a sequence, which contains some components twice, a checking and revision procedure is implemented. (The principle of revision procedure is to check that all components are included in the sequence. If they are not, the original instance is changed to the missing component.) For example; first crossover, then revision (only the heavy keys shown, not the separation methods):

1 4 3 2 –> 4 2 3 2 –> 4 2 3 1

4 2 1 3 –> 1 4 1 3 –> 1 4 2 3

3) Mutation of sequences at a randomly chosen location. Both the separation method and sequence is mutated.

4) Evaluation of sequences by using the fitness function which is based on the inherent safety index.

5) Selection of the best sequences and removal of worst and redundant sequences so that the size of population stays constant.

6) Steps 2–6 are repeated till the improvement during a certain interval is under the tolerance defined.

The size of initial population used in the genetic algorithm was 5 sequences. The size of crossover population was 2 sequences and the mutated population 2 sequences per generation. Consequently the total number of new sequences per generation was 4. The population size after selection was kept in 5.

The fitness function was based on the inherent safety index, which was simplified: It was noticed that there are only minor differences in the safety properties of the compounds in the process. Therefore most subindices are the same for all configurations. The equipment type used in all the configurations is the same (i.e. distillation). Therefore the subindex of equipment safety is constant too. Also the safety of process structures is quite the same since the distillation systems used are rather similar in configuration. Therefore the subindex for process structure was not evaluated and case-based reasoning was not needed.

The number of columns is changing however, if extractive distillation is used. Therefore the fluid inventory in the process becomes a major safety parameter. The inventory depends on the size of the columns in the process. It was assumed that all the columns have been designed for the same superficial vapor velocity. Therefore the column area is directly proportional to the vapor flow rate. Also it was assumed that the liquid hold up is proportional to the column area.

Therefore the total fluid inventory of the process is considered to be directly proportional to the total vapor flow of the columns. This is calculated by Equation 11 for each column.

The genetic algorithm reached the solution usually in ten generations in this problem of more than 1100 different solutions. A random optimization would require tens of generations. The best solution found is the first configuration (23 12 14 11) in Figure 13.

The results received form the optimization using inherent safety as the objective function are somewhat different compared to those calculated with an economic objective function earlier (Hurme, 1996). With the inherent safety objective function the simple distillations were favoured more than with the economic function. Exceptions are cases where the extractive distillation could improve separation very dramatically. This is because in simple distillations only one column is required per split, but in extractive distillation two columns are needed, since the solvent has to be separated too. This causes larger fluid inventory since also the extraction solvent is highly flammable. The results of the calculation are well justified by common sense, since one of the principles of inherent safety is to use simpler designs and reduce inventories to enhance safety.

14.4.2 Case Study; Emulsion Polymerization Process

As another case study a process synthesis of an emulsion polymerization process is given (Hurme and Heikkilä, 1998). In emulsion polymerization unsaturated monomers or their solutions are dispersed in a continuous phase with the aid of an emulsifier and polymerized. The product is a dispersion of polymers and called a latex. The raw materials are highly flammable unsaturated hydrocarbons and the reaction is exothermic which both cause a risk. The main phases and systems in an emulsion polymerization plant are listed in Table 31.

The aim of the reasoning is to determine the inherently safe process configuration for this process by using the Inherent Safety Index as an objective function in the genetic optimization. The index can be once again simplified, since the compounds present are fixed by the product produced. Therefore also the physical and chemical properties are fixed and the related subindices are constants. The subindices left as variables are the inventory, equipment safety, the safety of the process structure and the heat of reaction (per total mass of liquid present equipment) since this depends on the amount of inert phase present.

Table 31. The main phases and systems of an emulsion polymerization process (Kroschwitz, 1986).

1. Raw material unloading	2. Raw material storage
3. Feed and pretreatment systems *	4. Polymerization reactor*
5. Reactor heat transfer system*	6. Reactor safety systems *
7. Finishing operations	8. Monomer recovery
9. Vent treatment *	10. Latex storage and handling

Information on the safety properties, accidents, design recommendations and existing designs of the emulsion polymerization process was gathered from literature. Only the phases marked with asterisk (*) in Table 31 were considered. About 50 design recommendations or cases on the topic were found in the literature. A case base was formed of this information together with some general design recommendations. The cases were evaluated based on the safe process structure subindex, which was included into the cases in the database.

The main variables in the selected process phases were chosen and coded with integers for the synthesis procedure. These variables included the operation and equipment types used and how they are connected together. The 14 main variables chosen were the following:

1. Premixing
2. Preheating
3. Reactor type and mode of operation
4. Number of reactors
5. Reactor construction material
6. Reactor mixing
7. Baffles in reactor
8. Reactor heat transfer system
9. Method of liquid transfers
10. Relief system location
11. Relief equipment type
12. Reaction stopping method
13. Relief recovery system
14. Vent treatment equipment

The genetic optimization was started with an initial population size of five, which was generated randomly. The algorithm included crossover of two sequences, which were selected randomly. Also random mutations were done on two sequences. The number of mutations per sequence varied from four in the beginning to one in the end per sequence. The steps of the genetic algorithm are:

1. Random initial population size of 5

2. Crossover of two sequences randomly selected

3. Mutation of two sequences

4. Case-based reasoning on the safe process structure subindex

5. Calculation of fitness by using the inherent safety index. Only inventory, equipment safety, heat of reaction and process configuration subindices were considered.

6. Selection of the best sequences so that the population size stays in five.

7. Repetition of steps 2–7 till the improvement of fitness is below the tolerance given.

The procedure converged in less than 20 generations to an optimum. The optimum configuration had Inherent Safety Index value 16. The optimization started typically from a value 28–30. The inherently safest process alternative synthetized is shown in Figure 14.

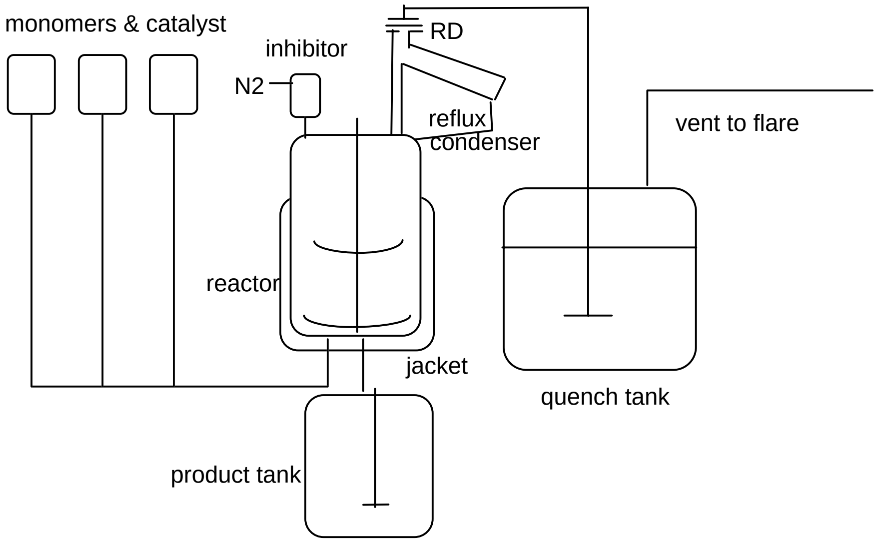

Figure 14. The synthesized emulsion polymerization system.

The process with the lowest inherent safety index value contain the following features: The process has a semibatch (instead of batch) reactor which results to a low monomer inventory in the reactor, since the reaction starts immediately when the first monomers are fed to the reactor. There is no premixing tank for the monomers, which would increase the inventory. Only one large reactor is used instead of several smaller to make the system simpler (i.e inherently safer process structure). Two mixers at one shaft are installed installed to increase the mixing efficiency when the liquid level in tank is changing. Also baffles are used for increasing the mixing efficiency. Cooling is accomplished by both the jacket and a reflux condenser. The reactor construction material is polished glad steel, which has better heat transfer properties compared to a glass-lined vessel. Liquid transfers to and from the reactor are accomplished by using elevation to reduce number of pumps (equipment safety). The relief system of the reactor includes a rupture disk, which is safer than a relief valve alone in the fouling conditions. The relief is led to a quench tank, which contains quench liquid to stop the reaction and to separate the liquid phase from the relief. This is safer than an ordinary knock-out drum or cyclone (safe process structure). The vent is led to flare system after the quench tank. Ordinary flare is used, since it has a larger capacity than a controlled collection system or a scrubber. An inhibitor addition to reactor is also included to stop the reaction chemically. This is a simple but possibly not always a reliable method (Fig. 14).

15. Conclusions

The aim of this doctoral thesis was to develop a method for inherent safety evaluation in preliminary process design. The motivation of the work has been an increasing need to evaluate the safety of processes in the early stage of process design partly because of government regulations and also for practical engineering reasons. To avoid hazards the studies of alternative features have to be carried out early in design, at the flowsheet stage and even earlier when it is decided which product to make and by what route. It is much easier to affect inherent safety in the conceptual design than in the later phases of process design. This is because the process route and other main selections are made in the conceptual phase. These decisions have a major effect on inherent safety. Also time and money is saved when fewer expensive safety modifications are needed and less added-on safety equipment are added into the final process solution.

The safety evaluation can be seen as a part of the process synthesis which includes economical, environmental and safety aspects. Different process alternatives have to be compared based on all of these criterias. Problems of the preliminary safety evaluations arise from the lack of information. To solve this problem a dedicated methodology for preliminary inherent safety evaluations is required.

In this thesis an inherent safety index for evaluating inherent safety in preliminary process design was presented. The inherent safety of a process is affected by both chemical and process engineering aspects. These have been dealt separately, since the index was divided into the Chemical Inherent Safety Index and the Process Inherent Safety Index. These two indices consist of several subindices which further depict specific safety aspects. The Chemical Inherent Safety Index describes the inherent safety of chemicals in the process. The affecting factors are the heat of the main reaction and the maximum heat of possible side reactions, flammability, explosiveness, toxicity, corrosiveness and the interaction of substances present in the process. The Process Inherent Safety Index expresses safety of the process itself. The subindices describe maximum inventory, maximum process temperature and pressure, safety of equipment and the safety of process structure.

The chemical and most process factors affecting the index are quite straightforward to estimate. More problematic are the equipment safety and the safety of process structure. The equipment safety subindex was developed based on evaluation of accident statistics and layout information. The evaluation of the safe process structure subindex is based on case-based reasoning, which requires experience based information on accident cases and on the operation characteristics of different process configurations.

The Inherent Safety Index can be calculated either for separate process sections or for the process as a whole with or without OSBL. The chemical and process categories can be used either together or separately. The individual factors may be emphasized differently depending on the company policies and the problem in hand. Thus different weighting of the factors may be introduced by the user, even a standard weighting based on expert ranking has been given. This approach allows a flexible and interactive comparison of process alternatives to be done in terms of inherent safety. It should be remembered that the various indices are relative not absolute quantities and they do not fully encompass all factors. To give an inherent safety profile separate subindices should be considered and not just the total index. The results should also be read with judgment.

In design it is typical that the same mistakes are done again since the use of available information is not organized. The use of case-based reasoning enhances the reuse of available experience, which reduces the possibility that the same errors are done more than once. In this work CBR was used for the evaluation of the inherent safety of process structure. The casebase was collected from design standards, accident documents and good engineering practice.

ISI can be used also as an objective function in computerized process synthesis. Process synthesis can be considered as an optimization task. Because the model is uncontinuous, ordinary optimization methods could not be used, but a genetic algorithm was employed instead. In a genetic algorithm the structure of the process was represented as a string of integers, which describes the operations required and how they are connected together.

At the moment the more intensive safety studies in process plant projects take mainly place in the late stages of design, when all what can be done is to add on protective equipment to avoid the hazard. Inherent safety designs will not come about without a change in the design process. This means making time available for the systematic study of alternatives during the early stages of design. The Inherent Safety Index assists the designers to choose inherent safety from the very start of process plant design. In fact this refers to concurrent engineering - an approach where design topics are considered more concurrently instead of the traditional sequential way.

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ISBN 951–38–5371–3 (soft back ed.)
ISSN 1235–0621 (soft back ed.)

ISBN 951–38–5372–1 (URL: http://www.inf.vtt.fi/pdf/)
ISSN 1455–0849 (URL: http://www.inf.vtt.fi/pdf/)